

ABSTRACT

Title of Dissertation: ENHANCED HYDROGEN PRODUCTION
FROM ACID GAS

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2017

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Hydrogen sulfide is a colorless, corrosive, toxic and flammable gas that is notorious for its nuisance rotten egg odor. Hydrogen sulfide endangers environment, human health and industrial equipment. Despite its high heating value, utilization of hydrogen sulfide as fuel is strictly prohibited using conventional combustion technologies. This malignant gas naturally exists in crude oil and natural gas wells. The separated-out hydrogen sulfide from crude oil and gas has other impurities that include: carbon dioxide, nitrogen, ammonia, carbonyl sulfide, carbon disulfide as well as benzene, toluene and xylene (commonly referred to as BTX). With the increase in energy demand, there will be reliance on utilization of sourer feedstock. Consequently, hydrogen sulfide stream needs to be efficiently treated.

On the other hand, hydrogen sulfide is considered a hydrogen rich feedstock. In addition, the hydrogen-constituted impurities, such as: methane, ammonia and BTX in the separated-out hydrogen sulfide stream from crude oil and gas furtherly enrich the hydrogen feedstock of this stream. Hydrogen can be produced from the decomposition

of hydrogen sulfide into its two valuable constituents: hydrogen and sulfur. Thermal decomposition of hydrogen sulfide was studied in this work. Experimental examination of wide range of several key parameters that affect the amounts of hydrogen produced and destructed hydrogen sulfide was conducted. Effect of inlet acid gas composition as well as role of different contaminant gases naturally accompanying H_2S on the chemistry, production of hydrogen and destruction of hydrogen sulfide were studied.

A chemical reaction mechanism that characterizes hydrogen sulfide thermal decomposition as well as decomposition of a mixture of hydrogen sulfide with methane over wide range of conditions was developed. The developed mechanism addresses the chemical kinetics and possible pathways. The difference in dominant reaction pathways between the two cases of presence and absence of impurities facilitated the identification of the role played by the contaminants.

ENHANCED HYDROGEN PRODUCTION FROM ACID GAS

by

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Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2017

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Dedication

To My Parents, Wife and Children.

Acknowledgements

The work presented in this dissertation is the result of my fruitful experience at the University of Maryland Combustion Laboratory. I am grateful to Prof. Gupta for offering me the opportunity to work at UMCL. As my mentor and advisor, Prof. Gupta provided me with continuing support and advice that helped shaping my research. He has motivated me to believe in the value of hard work, persistence and dedication to achieve excellence. I am also grateful to Prof. Ahmed S. Al Shoaibi for his insightful input on my research. . He offered valuable support in sourcing the finances used for this research investigation. My sincere appreciation also goes to members of my dissertation committee, Prof. Bao Yang, Prof. Kenneth Yu, Prof. Gary Pertmer, Prof. Nam Sun Wang and Prof. Dogxia Liu for their efforts, advice and support.

I thank my family for their unwavering support and encouragement. I am especially thankful to my father, Mr. Mahmoud El-Melih, and mother, Mrs. Salwa Er-Rashidy for their support, inspiration and all their love and encouraging to pursue my graduate degrees. I am also sincerely thankful my beloved wife, Ayatullah Ezz El-Arab, for all the support and all what she sacrificed to company me along in this journey. Also my son Aser and my daughter Ellaf for all the love and euphoria they filled my life with. They all deserve all the credit for my achievements. My gratitude to my family cannot be expressed in words.

I would like to extend my gratitude to the current and former team members of the Combustion Engineering laboratory for making the work environment enjoyable, and helping inside and outside the lab. I will never forget the sincere friendship and great memories I have had with all the Lab members. I would like to extend my thanks to

my friends and all of those who helped me and supported me along the path. I am blessed to have you all. No words would be enough to thank you properly.

Finally, I would like to express my deep gratitude to The Petroleum Institute, Abu Dhabi and ADNOC for their financial support of this project. I am also grateful to Reaction Design for their support to the numerical part of this research by providing a free license of CHEMKIN-PRO software

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Chapter 1: Introduction

This Chapter introduces hydrogen sulfide, its sources and its hazardous effects on both human health and environment. Then, brief description of current state-of-the-art technologies in treatment of hydrogen sulfide is provided. Later, objective of this research and motivations behind these objectives are addressed. Finally, the approach of this research and framework are briefly presented.

1.1. Hydrogen Sulfide and its Hazards

Hydrogen sulfide is a colorless, toxic, very corrosive and highly flammable gas that is notorious for its nuisance rotten egg odor. Hydrogen sulfide gas occurs both naturally as well as artificially in oil and gas refining industry. Hydrogen sulfide is a highly perilous gas that has deleterious effects on environment, human health. It also causes metals to become brittle which extends its adverse effects to utilized industrial equipment. This means special precautions should be taken when appropriately choosing or trimming equipment that is expected to encounter H_2S . Since utilization of sulfur-bearing fuels is forbidden, a hydro-desulfurization process of oil is an essential step in oil refining which removes all sulfur content in oil in form of hydrogen sulfide. Then, hydrogen sulfide has to be separated-out in an amine extraction process prior to utilizing natural gas as fuel. Therefore, petroleum-refining industry is the largest major artificial source of hydrogen sulfide. Hydrogen sulfide produced from hydrodesulfurization of oil products as well as the portion separated out from natural gas needs to be treated in a highly efficient process. Practically, hydrogen sulfide stream that is separated out has other impurities including: carbon dioxide, nitrogen, ammonia,

carbonyl sulfide, carbon disulfide, benzene, toluene, xylene (commonly referred to as BTX). Inappropriately, most of these impurities are neither environmental friendly nor human health friendly. Consequently, this malevolent stream cannot be vented to atmosphere instead, it must be treated. Given the high heating value of hydrogen sulfide and some of its impurities, utilization of such stream as fuel is an intuitive option. However, combustion of hydrogen sulfide and some of its impurities using conventional combustion systems is prohibited because formed products from this combustion process includes SO_x , which are the primacy antecedents of acidic rain. Other formed sulfurous-carbonaceous compounds (e.g., COS and CS_2), reach stratosphere and generate sulfate aerosol layer which could affect the ozone concentration negatively [1, 2]. For this reason, stringent environmental regulations are made and enforced on the permissible maxima of sulfurous emissions to be vented out to atmosphere from petrochemical plants [1, 3]. Accordingly, after separating out these gases in general and hydrogen sulfide in specific, an extremely efficient treatment process for sweetening petroleum products is necessary to meet the strict regulations. H_2S causes numerous hazards to the human health depending on concentrations and level of exposure. Low concentrations of H_2S can cause burning and tearing of eyes, headache, dizziness, dyspnea, and skin and throat irritations. Exposure to higher concentrations of H_2S can cause asphyxiation, loss of consciousness, and death. Health Administration (OSHA) classified the low-hazard H_2S exposure of 10 ppm or less [4]. The medium-hazard H_2S exposure was considered greater than 10 ppm and less than 30ppm [4]. Higher than 30 ppm was designated as high-risk H_2S exposure. They also stated that exposure to H_2S levels at 100 ppm or higher can endanger human life

immediately. On the other hand, BTX is not expected to be acutely toxic by the inhalation, oral, or dermal route of exposure. Breathing of vapors at concentrations above the recommended exposure standards of the components can cause central nervous system effects (e.g. drowsiness and lightheadedness) and, based on data on some of the components, inhalation of very high doses of BTX may cause skin and respiratory tract irritation. Prolonged and repeated exposure to high concentrations of BTX may cause serious health effects, including adverse effects in several organ systems, developmental toxicity and cancer [5].

1.2. Regulations on Sulfur Content in Fuels

In an effort to produce cleaner air with sulfur-bearing fuels, limits are placed on sulfur content in fuels and more stringent regulations on emission of pollutants from the combustion of H_2S and BTX are promulgated by various environmental regulatory agencies worldwide. The US EPA reduced the maximum allowable sulfur content in non-road diesel fuel from average of 3400ppm to 500ppm in 2007 and further to 15ppm in 2010. The highway diesel fuel was also reduced from current 500ppm down to 15ppm (per-gallon average) in June 2012 [6]. More recently, the US EPA announced a new regulation that mandates oil and gas refiners to reduce sulfur content in gasoline from the current limit of 30ppm down to 10ppm by 2017 [7]. A decade ago, the United States gasoline contained 300ppm of sulfur, but earlier regulations required refiners to cut the sulfur content by 90 percent, down to the current 30ppm.

The mobile source air toxics rules were also promulgated by the US EPA in 2007 to reduce benzene and other aromatics content in gasoline to further reduce hazardous air pollutants emitted by motor vehicles [7]. The major air toxics of concern

are BTX and other hydrocarbons such as 1, 3-butadiene, formaldehyde, acetaldehyde, acrolein and naphthalene. Oil and gas refineries are facing major challenges to meet the new fuel sulfur specification along with the required reduction of aromatics content. These requirements are expected to be more stringent in the future, therefore putting pressure on oil and gas companies to develop deep desulfurization processes and more environmentally-friendly technologies.

1.3.Separation of Acid Gases from Crude Oil and Natural Gas

1.2.1. Hydrodesulfurization

Hydrodesulfurization (HDS) is a commercially proven refining process that is traditionally used in refineries to reduce the sulfur content in fuels by passing a mixture of heated feedstock and hydrogen over catalysts - a Co-Mo or Ni-Mo charged catalytic column at high temperature and pressure - to remove sulfur as H_2S .

Typically, Conventional catalytic HDS method for reducing sulfur content involves catalytic treatment with hydrogen to convert the various sulfur compounds to H_2S and sulfur-free organic compounds at relatively high temperature range of 573 to 673 K and elevated pressure ranging from 30 to 130 atm.. Refineries desulfurize both distillate streams generated during direct distillation of crude oil and streams coming out from conversion units. In the HDS reactor, sulfur is reduced liberating H_2S which is then removed from the flue gas by amine scrubbing. Most HDS operations also remove nitrogen compounds and some metal impurities [8]. Refineries meet the ultra-low sulfur specifications on fuels that are produced from straight runs streams by controlling the hydrogenating conditions and selecting the appropriate catalysts. In

refineries, the H_2S resulting from the HDS reaction is eventually converted to elemental sulfur by a modified version of the Claus process which is described here in a later section [9].

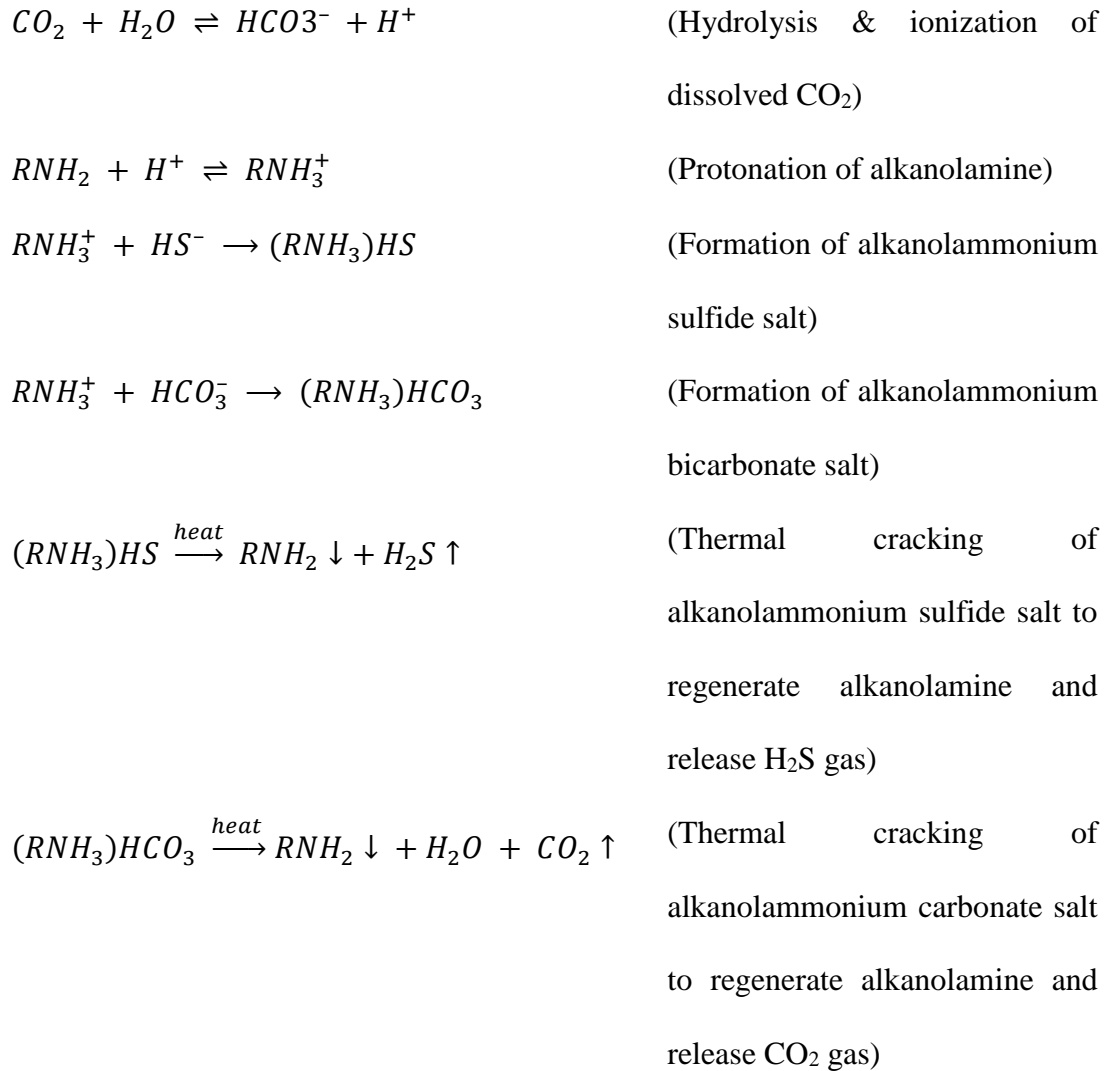
HDS is an expensive technology that is energy intensive and requires huge amounts of high purity hydrogen as reactant [10] [11]. Interest in HDS was initially triggered by the availability of hydrogen from catalytic reformers [8]. However, it is also widely acknowledged that HDS helps improve the fuel properties, as it favors a higher distillate to residual fuel oil ratio, in addition to the sulfur removal from crude oils [6, 7, 11]. This makes HDS more attractive in the light of increasing requirements for deep sulfur removal.

1.2.2. Amine Extraction Process

Separation of hydrogen sulfide gas from crude natural gas commonly takes place through the so-called “Amine extraction” process [2, 3, 12, 13]. This process involves the removal of acidic gases, mainly H_2S and CO_2 from crude natural gas and it is the main process in gas sweetening operations. In this process, The sour gas is up flowing through a tower, which contains an aqueous solution of alkaline-based organic compounds (alkanolamines) that consist of at least one hydroxyl and amino groups to produce sweetened gas stream (acid gas-free stream). This solution of alkanolamines is used to absorb hydrogen sulfide from crude natural gas [14]. This solution has an affinity for sulfur. Each of these two groups has its own role in the process, wherein the hydroxyl group reduces pressure of the vapor in the aqueous solution in order to increase the water solubility. On the other hand, the amino group provides the required alkaline medium in this aqueous solution in order to increase the tendency of the acidic

gases absorption. The most common, which have been widely used commercially, are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) [12]. Amines, which contain two hydrogen atoms attached to the nitrogen atom, are called primary amines such as (MEA), while amines that contain only one hydrogen atom attached to the nitrogen atom are called secondary amines such as (DEA), and the amines that contain no hydrogen atoms are called tertiary amines such as (MDEA) [13]. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. The amine solution used can be regenerated (that is, the absorbed sulfur is removed), allowing it to be reused to treat more sour gas. During the separation of H₂S and CO₂, small concentrations of methane, organic sulfides and BTX often accompany the separated gas. In addition to hydrogen sulfide and carbon dioxide, acid gas can contain nitrogen existing as part of ammonia in the aqueous solution, which is converted into nitrogen and water. Separation process starts with the ionization of H₂S and CO₂, alkanolamine protonation, and formation of sulfur and bicarbonate salts. Formed salts are cracked thermally to regenerate the alkanolamines and decouple both H₂S and CO₂. The following set of reactions describes the amine extraction process of both hydrogen sulfide and carbon dioxide from crude natural gas stream [15]:





1.3. Treatment of acid gas (Claus Process)

Limits on sulfur content in fuels and an effort to produce cleaner air with sulfur bearing fuels, more stringent regulations on emission of pollutants from the combustion of hydrogen sulfide are set by various environmental regulatory agencies worldwide. Hydrogen sulfide is present in most natural gas wells, and as light and sweet feedstock is becoming increasingly scarce, there is a shift towards utilization of heavier and sourer feedstock with higher content of hydrogen sulfide to meet the increasing demand

on energy. Most often, in addition to H_2S , this feedstock contains various contaminants, such as carbon dioxide, nitrogen, ammonia, organic sulfides and higher aromatic hydrocarbons, such as BTX. Combustion of any crude natural gas containing the aforementioned contaminants results in the formation of highly toxic compounds (such as, SO_2 , H_2SO_4 , CO , COS and CS_2 amongst other compounds). Therefore, it is a necessity to separate out and treat hydrogen sulfide and other contaminants from crude natural gas.

The collected acid gas even in small amount must be treated to hinder its harmful effects on human health and environment. The currently most widely employed technology is the well-known Claus process [12, 16] that is used for the sulfur recovery while treating hydrogen sulfide. Different sulfur recover processes are in commercial operation as well such as: Selectox, Stretford process, Unisulf process [17]. Also novel chemical looping approach has been developed for sulfur recovery. The selection of the acid gas treating process depends on many design consideration that includes: operating pressure, temperature, space velocity, sulfur recovery levels, types, types and concentrations of impurities, amount of hydrogen sulfide content in the stream, required quality of sulfur recovered and regulations on emission of sulfur to be met. Among all sulfur recovery processes, modern modified Claus process is the most mature and reliable technology with highest efficiency of 97-98%.

Practically, Claus process is divided into two stages of a thermal stage followed by multiple catalytic stages as shown on Figure 1. The catalytic stages can be several due to high level of sulfur capture efficiency required from the gases.

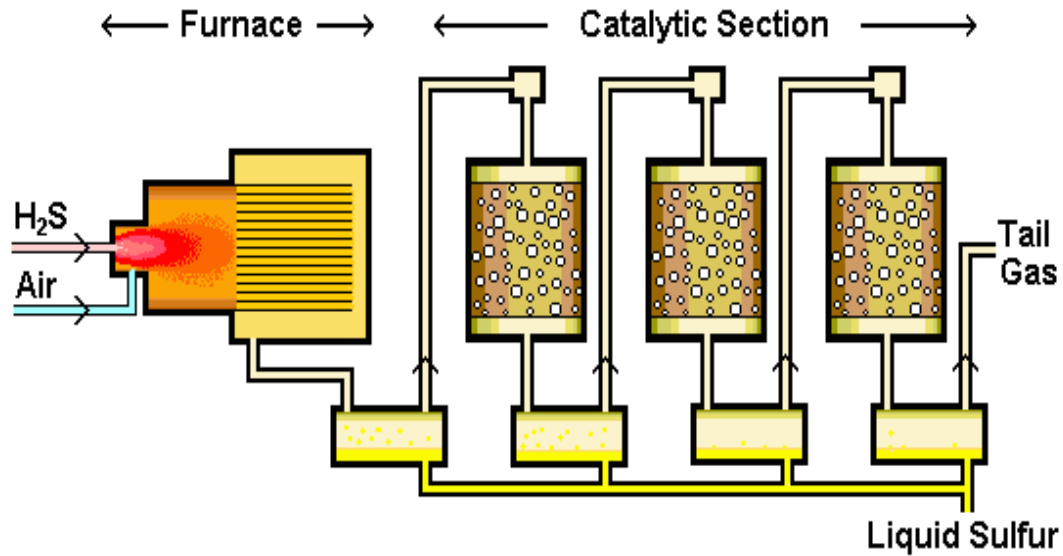
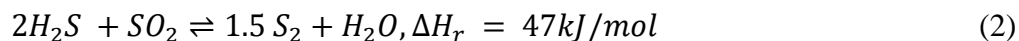
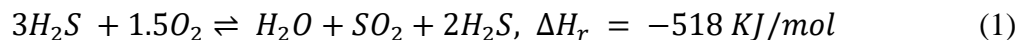


Figure 1. The Claus Process [12]

1.3.1. Thermal stage of Claus Process

In Claus process, reaction between H_2S and O_2 occurs under fuel-rich conditions (at equivalence ratio of $\Phi = 3$) where partial oxidation of H_2S to form sulfur oxides. The products from this step are: sulfur dioxide, water and unreacted hydrogen sulfide. Additionally, some of the sulfur dioxide produced here reacts with remaining hydrogen sulfide inside the furnace to produce elemental sulfur and steam according to reaction (2) shown above. The products from the furnace flow into a waste heat boiler to condense the sulfur. The acid gas/air mixture is passed into a furnace operating at temperatures from 1027-1477 °C; where the reactions are allowed sufficient time to reach equilibrium. However, these reactions occur in two stages as described below in equations 1 and 2.



The efficiency of Claus reactor wherein both the energy and sulfur recovery occurs can vary significantly depending on the acid gas composition, reactor design configuration and operational conditions. Acid gas composition varies significantly depending on the natural gas well, and greater variation could even occur as the world is shifting towards utilization of heavier and sourer feedstock with higher content of acid gas and other contaminants due to depletion of light and sweet feedstock. As a result, there is significant demand for improved energy and sulfur recovery efficiency in both new and existing gas processing plants and refineries, while reducing health and environmental burden. This will help maintain cleaner air with sulfur bearing fuels and also meet the strict regulations that are promulgated by various environmental regulatory agencies worldwide on the discharge of acid gas and hazardous by-products of its combustion.

1.3.2. Catalytic stage of Claus process

The reactions in the catalytic stages are the same as that in the thermal stage but with reactions occurring at a lower temperature. The remaining H_2S from the Claus furnace reacts with the SO_2 at lower temperatures (about 470-620 °C) over an alumina- or titanium dioxide-based catalyst to form additional sulfur. In the catalytic stage, mostly S_8 is produced, which is an exothermic reaction whereas in the thermal stage S_2 is the major product [18, 19]. Other allotropes of sulfur may also be present in smaller quantities. About 60-70% of elemental sulfur, on the average, is produced from reaction 2 [18]. Reaction 2 is exothermic and a cooling stage is needed following these steps in order to condense the sulfur produced. The condensed phase is then separated from the gas stream by draining it into a container.

The basic Claus process has a sulfur recovery efficiency of about 94% to 98% (Sulfotech). However, many improvements have been developed and the modified Claus process achieves 99+% of H₂S conversion efficiency.

1.4.Motivations and Objectives

With the malignant effects hydrogen sulfide has on both human health and environment, separation of hydrogen sulfide from sulfur bearing fuels, crude oil and crude natural gas followed by a highly efficient treatment process is crucial to thwart its adverse effect.

The current increase in energy demand around the world with the shrinking reserves of fossil fuels, exploitation of sourer feedstock (higher content of hydrogen sulfide) will be an option to meet the increase in demand.

The current utilized technology is Claus process, which relies mainly on the combustion of hydrogen sulfide, does not allow for presence of other contaminants such as carbon dioxide, BTEX and hydrocarbons higher than C₃. These contaminants affect the process adversely; it deteriorates the quality of sulfur, lead to formation of undesired sulfurous compounds in addition to affecting the efficiency of the process itself or require more catalytic stages which imposes immense cost.

Acid gas does not contain hydrogen sulfide only, carbon dioxide, nitrogen, BTEX, C₁ – C₄ hydrocarbons and ammonia often exists in acid gas. Although some of these gases are not hazardous, their existence in the inlet stream affect H₂S decomposition process significantly.

During the process of reforming hydrogen sulfide contaminated by other gases that naturally accompanying hydrogen sulfide, other sulfurous compounds forms that

are also hazardous to human health and environment, consequently terminating sulfur derived species demands understanding the conditions under which these compounds are formed and the optimum conditions under which such compounds can be minimized or better eliminated.

The very strict regulations made on the maximum allowable sulfur emissions requires an extensive cleanup process of the tail gases, so that if the regulations became more stringent the feasibility of Claus process cannot be sustained by sulfur recovery only.

All of the abovementioned motivations have molded the objectives of our research. The major objective of this research is to understand the chemistry of thermal pyrolysis of sole hydrogen sulfide. Based on this understanding a comparison between thermal decomposition of hydrogen sulfide and pyrolysis of hydrogen sulfide with presence of various contaminants including: BTX, ammonia, methane, nitrogen under different reaction conditions can reveal the role played by each contaminant. The role of other key parameters that will be determined, this includes:

- Effect of temperature
- Effect of inlet gas stream composition
- Effect of presence of other contaminant gases in different amounts

A hybrid approach of experimental and numerical will be followed with main stream of research of experimental approach to identify and quantify the products of the pyrolysis reaction in both cases of pure hydrogen sulfide or contaminated hydrogen sulfide.

Developing a reaction mechanism that characterizes the pyrolysis of hydrogen sulfide that assists in identification of the most dominant chemical kinetics pathway by numerically modelling the experimental data obtained is another objective.

1.5. Research Framework and Organization of the Dissertation

Framework of research presented in this study comprises various approaches to achieve the targeted objectives.

The first approach was experimental and it aimed to investigate experimentally the role of several key operating conditions, i.e., reactor temperature and inlet gas composition, on amounts of hydrogen produced and destruction of hydrogen sulfide by measuring the stable end products of hydrogen sulfide thermal decomposition reaction.

The second approach was to investigate the role of different contaminant gases that are naturally accompanying hydrogen sulfide on chemistry of the reaction, production of hydrogen, treating hydrogen sulfide and formation of other sulfurous species during the reaction. This is also done experimentally wherein different concentrations of different gases have been injected individually along with hydrogen sulfide and the formed species from these reactions have been identified and their concentrations have been measured.

The final approach was numerical with objective to develop a detailed reaction mechanism that has aptitude to characterize the pyrolysis of hydrogen sulfide under wide range of operating conditions. Reactions between hydrogen sulfide and other contaminant gases have also been included to represent the reformation of hydrogen sulfide in the presence of other contaminants. The developed mechanism has been also

used to understand the chemistry of H_2S and identify the dominant chemical kinetics pathways and reactions in H_2S decomposition.

The organization of the succeeding chapters will be as follows:

Chapter 2: a review of previous work carried out on thermal decomposition of hydrogen sulfide. The presented literature review presented in this chapter can be categorized into 3 main streams: Experimental kinetic studies of non-catalytic thermal decomposition of hydrogen sulfide stream, Modeling of kinetics of hydrogen sulfides thermal pyrolysis, Developing a catalyst for the reaction.

Chapter 3: experimental facility design and diagnostics to be used for achieving goals of this study.

Chapter 4: results and discussion. Results on experimental investigation of effect of temperature, inlet composition, presence of impurities have been presented.

Chapter 5: conclusions from the research conducted throughout this study and contribution from this work in the literature are addressed.

Chapter 6: Recommendations for future work on the field of production of hydrogen from hydrogen sulfide are made to improve the understanding of the chemistry of sulfur.

Chapter 2: Literature Review

In this section, an overview of the available literature related to the research topic of this dissertation is presented. Available literature lies within the scope of our research has been categorized into four sections. The first section highlights practical problems of sulfur recovery in industry followed by discussions on alternative ways with focus on hydrogen and sulfur recovery. The second section summarizes previous efforts by investigators on non-catalytic thermal decomposition of hydrogen sulfide. These investigations include both contributions of investigators in the development of detailed/reduced reaction mechanisms for hydrogen sulfide combustion and pyrolysis as well as experimental characterization of the reaction process. The third section covers investigations on reaction of hydrogen sulfide with contaminants naturally accompanying hydrogen sulfide with highlights on the chemistry of pyrolysis of these contaminants. The forth section discusses the techniques employed in shifting equilibrium limit on hydrogen sulfide pyrolysis. The fifth section provides insight on catalysts developed for accelerating the cracking reaction of hydrogen sulfide and evaluating the performance of these catalysts. It is also vital to emphasize that this chapter sheds light only on the available previous work that has been found, from our point of view, related to the research presented in this dissertation.

2.1.H₂S Treatment, Challenges and Alternatives

As previously introduced, hydrogen sulfide is a toxic gas not only to human health but its adverse effects extend to environmental health and equipment functionality. It can be inferred that the sulfur constituent in hydrogen sulfide is the

source of all the problems accompanying this gas. For this reason, the intuitive option to mitigate the impact of hydrogen sulfide is to extract its sulfur constituent. Many technologies have been utilized to recover sulfur from hydrogen sulfide. These technologies include: Amoco direct oxidation, LO-CAT, Selectox, Stretford, Unisulf and Claus. All of these technologies have their advantages and limitations [17]. Sometimes, they are used in complementary setting. Among these processes, Claus process is the most mature technology in the field of sulfur recovery. Details on Claus process have been discussed earlier. These technologies aim to extract sulfur constituent from hydrogen sulfide so that the effluent products are more environmental friendly. Meanwhile, recovery of sulfur as an important mineral that is in demand in many industrial applications include sulfuric acid production, fertilizers, fungicide and pesticide, food preservation and pharmaceuticals industries. With the growing awareness of environmental health and enforcement of stringent environmental regulations, the current exploited processes for sulfur recovery may lose its economic feasibility in case its operation cost and tail gas clean up exceeds the value of sulfur recovered under the new regulations [20, 7]. In addition, the unavoidable production of hydrogen sulfide from gas plants, refineries and other plants that must be properly treated is increasing with the increase in energy demand. This brings the attention to the other valuable constituent in hydrogen sulfide that have the potential to foster the economic feasibility of the treatment process.

Efforts to produce both hydrogen and sulfur from hydrogen sulfide have been made in recent years through a diverse variety of technologies. These involve thermal,

thermochemical, electrochemical [21, 22], photochemical [23, 24, 25, 26] and plasmochemical methods [27, 28, 29, 30, 31].

The only drawback of the alternative of cracking of H_2S is the high energy requirement for this reaction and the relatively lower conversion of hydrogen sulfide compared to the modified Claus process. However, the most direct process of obtaining hydrogen and sulfur from hydrogen sulfide is thermal decomposition, catalytically or non-catalytically. The challenge faced in this method is that the reaction is highly endothermic and is equilibrium limited even at high temperatures which can be translated to high thermal energy input requirements. Since thermal energy is one of the main products of Claus process, hybrid operation of Claus process has been suggested where sulfur being recovered and thermal energy is supplied to dissociation of hydrogen sulfide stream. Hence, interest in thermal decomposition of hydrogen sulfide has grown and many scientists directed their research to thermal dissociation of hydrogen sulfide. Another area of research that was open is the catalytic thermal dissociation of hydrogen sulfide with the aim to reduce the energy requirement for this reaction.

In addition, many techniques have been employed to shift equilibrium limit on decomposition of H_2S using several methods such as preferential removal of products of reaction by membranes or adding some different material that react with one of the products then the equilibrium shifts towards more consumption of H_2S

Another method to overcome the high endothermicity and equilibrium limitation was two-step processes such as the sulfurizing of a transition metal or a lower

sulfide to liberate the hydrogen and then calcining the higher sulfide to decompose into sulfur and the original metal or sulfide have been proposed [20].

2.2. Thermal Ddecomposition of Hydrogen Sulfide

To produce the sulfur oxide required for the Claus reaction to occur, partial oxidation of hydrogen sulfide under rich conditions occurs in the thermal stage of Claus process. For this reason, interest in studying chemistry of sulfur in flames has grown. Combustion of hydrogen sulfide has been examined experimentally [32, 33, 34, 35, 36, 37, 38] as well as numerically [39, 19]. Moreover, many researchers focused early on studying the major features of hydrogen sulfide flame such as: flammability limits [40], ignition delay [41], chemical equilibrium [42], and flame speed [43].

Interest in hydrogen sulfide pyrolysis has been focused on later as part of the reactions occurring in Claus process. Then, it has been focused on as a separate area of research with objective of hydrogen production. The literature available on thermal decomposition of hydrogen sulfide can be categorized as follows:

1. Experimental kinetic studies of non-catalytic reaction.
2. Modeling of kinetics of hydrogen sulfides thermal pyrolysis

Studies on the non-catalytic thermal decomposition of H_2S (reaction 3) and the reverse reaction between hydrogen and sulfur have been reported by a number of researchers in the open literature. These studies have extensively examined the kinetics of this equilibrium system from both the forward and reverse reaction directions, over a wide range of temperatures.



Recent studies have also cited interest in the kinetics of these processes at higher temperatures, as it relates to thermal cracking of H₂S [44, 45, 46]. Despite this type of information in the open literature, the reported studies, so far, have not provide a unified picture of the overall kinetics within this system, often yielding conflicting results even as to the form of the rate expressions, see Table 1.

Table 1. Kinetics parameters for thermal Pyrolysis of hydrogen sulfide

Rate equation	Activation Energy (forward reaction) [kJ/mol]	Catalyst	Temperature range [K]	Ref. no.
$r = k_1 p_{H_2S} - k_2 p_{H_2} p_{S_2}^{\frac{1}{2}}$	196	None	873-1133	[47]
$r = k_1 [H_2S] - k_2 [H_2][S]^{\frac{1}{2}}$	217	None	1061-1201	[20]
$r = k_1 p_{H_2S} p_{S_2}^{\frac{1}{2}} - k_2 p_{H_2} p_{S_2}$	188	None	1123-1423	[46]
$r = k_1 p_{H_2S}$	241	None	1030-1070	[48]
$r = k_1 [H_2S] - k_2 [H_2][S]^{\frac{1}{2}}$	286	None	1350-1600	[49]
$r = k_1 [H_2S][S]^{\frac{1}{2}} - k_2 [H_2][S_2]$	131.3	None	875-1563	[50]
$r = k [H_2S]^2$	75.7	Alumina	933-1073	[51]
$r = k [H_2S]^2$	90.0	Alumina	933-1073	[52]
$r = k [H_2S]^2$	49.8	Alumina	773-873	[53]

Darwent and Roberts [54] a second order dependency on H₂S for the rate of decomposition reaction, whereas both Raymont [44] and, more recently, Adesina et al. [48] have suggested first-order kinetics. In a study of non-catalytic H₂S decomposition, Kaloidas and Papayannakos [47] provided a reversible kinetic treatment of the system. These authors, however, implicitly relied on the available kinetic models within the literature. For their model they used a first-order kinetics for the H₂S decomposition reaction and, $-\frac{d[H_2]}{dt} = k[H_2][S_2]^{\frac{1}{2}}$, for the rate expression of the reverse H₂/S₂ reaction first proposed by Aynsley et al. [55] at lower temperatures, containing terms first order in H₂ but half-order in S₂. The reverse reaction involving H₂ and S₂ was extensively studied by Dowling et al. [50] over the temperature range from 600 to 1300 °C. They reported an experimental rate expression for this reaction different from that used by Kaloidas and Papayannakos [47]. The form of the rate expression given by these authors was, $-\frac{d[H_2]}{dt} = k[H_2][S_2]$, that contain terms that are first order for both H₂ and S₂. As part of this study a reversible kinetic treatment of the system was also performed that included the assumption of strict first order kinetics for H₂S decomposition and pseudo-first order behavior for the H₂/S₂ reaction for the conditions examined.

The high-temperature decomposition of H₂S has been studied (Randall and Bichowsky [56], Raymont [44], Fukuda et al. [57], Chivers et al. [58]). Direct investigation of the reaction between hydrogen and sulfur is only reported in the literature at lower temperatures. In light of the apparent lack of agreement on the kinetics of this system evident from the literature, a reevaluation of the kinetic data for the H₂/S₂ reaction reported in the study by Dowling et al. was undertaken. However,

Dowling et. al. [50] extended this study to Claus Process conditions (high temperature range of 602-1290 °C and residence time between 0.03-1.5s) and reported first-order dependence on both hydrogen and sulfur for the reversible homogenous gas-phase kinetics of H_2S decomposition to hydrogen and sulfur. They also examined the re-association of hydrogen and sulfur and showed the feasibility of using a rapid thermal quenching technique to minimize the reverse reaction of H_2S decomposition (reaction 3).

Most of these studies were carried out at temperatures ranging up to about 1200 K. At 1200 K and 100 kPa, less than 20% of H_2S is dissociated at equilibrium. Lower pressures and higher temperatures increase the degree of dissociation.

Hawbolt et al. [46] studied pyrolysis of H_2S in the temperature range of 1123-1423 K under Claus condition, and determined a pyrolysis rate expression for H_2S . They reported that H_2S dissociation is minimal at temperatures below 1273 K. This substantiates the need for high temperatures in the Claus thermal reactors.

Thermal decomposition of Hydrogen Sulfide was studied by Kaloidas and Papayannakos [47] in a non-isothermal flow reactor at pressures of 131-303 kPa and temperatures of 873-1133K at specific flow rates of 3.4-36.0 mol/m²s. The reactor was a fused-alumina tube of internal diameter 6 mm and length 403 mm. The temperature distribution inside the reactor along its length was measured by a traveling thermocouple. The flow rates used satisfied the plug flow requirements. Filling the reactor with crushed alumina pieces (same material as reactor) having 15-fold larger surface area than the reactor wall did not affect the conversion, indicating that the reactor material did not act as catalyst. The variables studied were temperature,

pressure and (space) velocity. Based on that, an empirical rate equation describing the overall reaction as the difference between the rates of the forward reaction and the reverse reaction was fitted to the conversion data. Activation energies of 196 and 105 kJ/mol were obtained for the forward and reverse reactions, respectively.

Adesina et al. [48] used a quartz tube plug flow reactor at temperatures to address the kinetic aspects the thermal pyrolysis of hydrogen sulfide over a temperature range of 1030 to 1070 K. at such temperature hydrogen production is not significant. Also reaching equilibrium limit, at these relatively lower temperatures, takes longer residence time which mean that he might acquire kinetic data but cannot reach equilibrium. The hydrogen sulfide stream was diluted with argon over a wide range of concentrations (20-100% H₂S). The quartz tube reactor was housed inside an electrical furnace equipped with a temperature controller. Blank experiments with a telescopically arranged thermocouple showed the axial temperature variation and the temperature difference between the average temperature and the set temperature over the reactor length was relatively small, of the order of few degrees. They reported that hydrogen yield also increased monotonically with hydrogen sulfide feed concentration at all temperatures and the reaction is first order in hydrogen sulfide partial pressure. Experiments showed that the activation energy for H₂ production of 200 kJ/mol is lower than that for the global decomposition reaction of about 241 kJ/mol.

Since decomposition reaction are favored at high temperature and low pressures, Bandermann and Harder [52] carried out the decomposition reaction in a quartz reactor with alumina as catalyst over temperature range of 1090-1230K and 13-51 kPa pressures. Equilibrium conversions were obtained at all conditions in less than

20ms. The amount of catalyst was 2.25g and the flow rate range was 0.03-0.10Nm³/h. To hinder recombination, the reaction products were quickly cooled down to 700 K after leaving the reactor. The sulfur was removed by condensation in a heat exchanger followed by an electro-filter. A pressure swing adsorption system was designed to separate the gas containing 25-30% hydrogen and 75-70%hydrogen sulfide. A commercial plant was proposed combining the low-pressure decomposition, sulfur condensation and pressure swing adsorption to operate the hydrogen product and recycle the un-reacted H₂S.

Harvey et al. [49] studied thermal dissociation of hydrogen sulfide at temperatures from 1350 to 1600 K and pressures from 15 to 30 kPa in an alumina reactor. They decided this range of temperature since the dissociation rates at temperatures which are attractive for an industrial process are not well-characterized. Since alumina has catalytic effect on thermal dissociation of hydrogen sulfide, they used different reactors of alumina with different surface area to volume ratio. Then they extrapolated the effect of the area to zero area, which corresponds to the homogeneous gaseous phase reaction regardless of the effect of the catalyst. This approach enabled them to present a global reaction rate expression that includes surface and gas phase contribution. They found that the surface reaction is the dominant contributor with activation energy for the forward surface reaction of 194 kJ/mol.

Tetsuo et al. [59] measured rate of formation of S₂ during the pyrolysis of H₂S in shock waves by UV absorption technique in the temperature range of 2380-3000 K. at all the temperature measured, the S₂ absorption during the reaction could be represented

$$(S_2)_t = (S_2)_\infty \{1 - \exp(-kt)\}$$

Where $k = 10^{9.2} \exp\left(-\frac{72 \text{ kcal}}{RT}\right) \text{ s}^{-1}$

However, they could not identify exactly which reaction is the dominant reaction in S_2 formation. However, they deduced that the straightforward reaction of $S_2 \rightleftharpoons 2 S$ is not the main dominant reaction. The mechanism of the formation of S_2 was proposed and the value of the second order rate constant, k_1 , for the primary reaction, $H_2S + M \rightarrow SH + H + M$, was estimated as follows:

$$k_1 = 10^{13.1} \exp\left(-92 \frac{\text{kcal}}{RT}\right) \text{ l mol}^{-1} \text{ s}^{-1}$$

The effects of the addition of NO and O_2 on the rate of S_2 formation were also investigated. They found that NO acts as radicals scavenger. On the other hand, O_2 promotes the formation of S_2 .

Bowman and Dodge [60] studied thermal decomposition of H_2S behind incident shock waves in H_2S -Ar mixtures over the temperature range 2700–3800°K for total concentrations in the range 2×10^{-6} to 7×10^{-6} mole/cc. They monitored H_2S concentration using an ultraviolet absorption spectroscopic technique, and the S-atom concentration was inferred from measurements of the absolute intensity of emission from electronically-excited S_2 . Detailed information on the decomposition mechanism was obtained by comparing measured H_2S and S-atom concentration profiles with results from a computer simulation of the reaction. During the decomposition reaction, measured concentration profiles could be modelled adequately using a six-reaction mechanism. For the conditions investigated, they could infer that the primary decomposition step was shown to be $H_2S + M \rightleftharpoons SH + H + M$ and this reaction is

second-order with a rate coefficient, for argon as a collision partner, given by $K_1^{Ar} = 10^{14.3} \exp(-310 \text{ kJ}/RT) \text{ cc/mole} \cdot \text{sec}$.

Woiki and Roth [61] also studied thermal decomposition of 5-100 ppm H_2S diluted in Ar behind reflected shock waves at temperatures $1887 \text{ K} \leq T \leq 2891 \text{ K}$ and pressures around 1.3 bar by applying atomic resonance absorption spectroscopy (ARAS) for time-resolved concentration measurements of H and S atoms. Both the S and H concentration profiles showed almost linear increases at early reaction times with the S atoms exceeding the H atoms by a factor of 10-20.

Therefore, reaction $\text{H}_2\text{S} + \text{M} \rightleftharpoons \text{H}_2 + \text{S} + \text{M}$ (with rate coefficient k_1), was regarded as the initial step in the H_2S decomposition contrary to public belief that $\text{H}_2\text{S} + \text{M} \rightleftharpoons \text{H} + \text{SH} + \text{M}$ is the dominant initiation reaction. The rate coefficient k_1 was determined from the slope of the early S concentration profiles to be $k_1 = 1.9 \times 10^{14} \exp(-32860 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The subsequent reaction between H_2S and S atoms, $\text{H}_2\text{S} + \text{S} \rightleftharpoons \text{products}$ (with rate coefficient k_2), was investigated in two different manners: first by evaluating the quasi-stationary S concentrations observed at longer reaction times in pyrolysis experiments of 100 ppm H_2S and second by monitoring the decay of photolytically generated S atoms in laser flash photolysis-shock wave experiments with 30 ppm CS_2 and 50-150 ppm H_2S . Both groups of experiments covered the temperature range $1340 \text{ K} \leq T \leq 2120 \text{ K}$ and result in a rate coefficient $k_2 = 5.7 \times 10^{14} \exp(-7600 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. H concentration profiles measured during $\text{H}_2\text{S}/\text{Ar}$ pyrolysis were analyzed using a simplified reaction mechanism, which was able to predict the experimental findings. In that case it was

necessary to introduce a reaction channel $H_2S + S \rightleftharpoons HS_2 + H$, forming the reaction products HS_2 and H , with an efficiency of 35-57% of the overall reaction.

Olschewski [62] studied thermal decomposition of H_2S in shock waves by monitoring UV absorption signals in the range 210-330 nm. Following the decay of H_2S at 215 nm, experiments with 200-5000 ppm of H_2S in Ar could be analyzed. First-order rate constants of $k/[Ar] = 4.0 \times 10^{14} \exp(-33000 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were obtained between 1800 and 3300 K. As these results complement observations on the formation of S atoms by Woiki and Roth [61] the thermal dissociation of H_2S is proven to proceed by the following spin-forbidden elimination reaction: $H_2S + M \rightleftharpoons H_2 + S(^3P) + M$ with a rate constant k_1 which is given by $k_1 = k/2$, i.e., $k_1/[Ar] = 2.0 \times 10^{14} \exp(-33000 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 1800 and 3300 K. The measured rate constants are analyzed in terms of unimolecular rate theory, and a threshold energy of $E_0 = 295 \text{ kJ mol}^{-1}$ is derived which agrees with the endothermicity of the above reaction.

Karan and coworkers [63] obtained new kinetic data for the hydrogen sulfide decomposition reaction from quartz tubular reactors over a temperature range of 800-1250°C are reported. They deduced that the global hydrogen sulfide thermal decomposition reaction has a first-order dependency on H_2S concentrations at these temperatures. The regression of their experimental data gave an overall hydrogen sulfide decomposition reaction rate constant as $k \left[\frac{\text{m}^3}{\text{kmol.s}} \right] = 1.68 \pm 0.86 \times 10^{11} \exp[(28,940 \pm 840)/T]$. Moreover, the main finding of this work was the reconciliation of kinetic data between higher temperature (1500-3100°C) shock tube studies (Olschewski et al., [62]; Woiki and Roth [61]) and kinetic data from the lower

temperature flow reactor studies represented by their work. A single rate constant for H_2S decomposition reaction, $k \left[\frac{\text{m}^3}{\text{kmol.s}} \right] = (1.12 \pm 0.11) \times 10^{11} \exp \left[\left(\frac{28,360}{T} \right) \right]$ was found to represent satisfactorily the three sets of data over a wide temperature range of 800–3,100°C.

Faraji et al. [64] investigated thermal noncatalytic decomposition of H_2S in the temperature range 1000–1200°C, admixed with nitrogen or helium at a total pressure of one atm. It has been found that, contrary to earlier literature claims, the inhibiting effect of the back reaction, the reverse reaction between H_2 and S_i ($i = 1-8$) molecules to regenerate H_2S , can be overcome by the use of readily attainable, sufficiently high gas flow rates. In agreement with thermodynamic predictions, the reaction has been shown to be temperature and H_2S pressure dependent; the experimental conversion was found to increase with rising temperature and declining H_2S pressure. At 1200 °C and one atm. H_2S pressure, the measured conversion was 35.6% corresponding to 97.5% of the thermodynamic limit when a steady gas flow of 50 mL/min and residence time of 48 seconds were maintained. The highest experimental conversion, 65.8%, was obtained at the highest temperature, 1200 °C, and lowest pressure, 0.050 atm., employed. For optimum conversions under the present experimental conditions, it was necessary to use a quartz reactor packed with quartz chips. Apparently, at 1200 °C the chips have no catalytic effect but serve as heat transfer agents.

Since thermal decomposition of hydrogen sulfide is known to be endothermic with high energy intensive requirement, Slimane et al. [65] investigated numerically partial combustion of hydrogen sulfide under super-adiabatic conditions and ultra high equivalence ratio for hydrogen production. They have examined different acid gas

compositions and oxidizers (20% H₂S, 80% N₂)/air, (20% H₂S, 80% N₂)/O₂, 100% H₂S/air, 100% H₂S/O₂, (25% H₂S, 75% N₂)/air, and (25% H₂S, 75% N₂)/O₂. The focus of the study was to optimize the hydrogen yield under all examined conditions. The results revealed that high H₂ and low SO₂ yield were achieved under ultra-fuel-rich conditions (equivalence ratios above 6). Using oxygen as an oxidizer shifts the favorable conditions of high H₂ yield to higher equivalence ratios above 12. This is similar to reactions happening in Claus process except that the equivalence ratio is higher. The ultra-rich mixture utilizes the heat released in the exothermic reaction to decompose the unburnt hydrogen sulfide.

In addition to experimental examination, chemical reaction mechanisms were developed and validated numerical simulations were conducted.

Sendt et al. [66] constructed detailed chemical reaction mechanism to describe reactions in the H₂–S₂–H₂S system based on the close resemblance of H₂–O₂ system. Their mechanism comprises 21 reactions among the species H₂S, S₂, H₂, HSSH, HSS, SH, S, and H. Rate constants for few reactions were taken from experimental values available in literature, but the kinetics of most of the reactions have been studied theoretically using a combination of transition state theory for bimolecular reactions, master equation calculations for unimolecular decompositions, and QRRK methods for chemically activated reactions. The mechanism has been validated against a diverse collection of published data for H₂S pyrolysis in batch or in flow reactors, for temperatures ranging from 873 to 1423 K, pressures from 0.04 to 3 bars, and H₂S mole fractions from 0.02 to 1. The predictions of the mechanism are sensitive only to the rates of the processes responsible for S–S bond formation as in the following reactions



Slight adjustment of these rates was made for the data to be modeled accurately. Data for the reverse, hydrogen sulfurization reaction ($H_2 + S_2$) are also modeled very accurately. This comprehensive chemical kinetic mechanism for the H/S system was the first step for construction of accurate models for H_2S oxidation in combustion and related systems.

Bionist et al [67] studied the kinetics of Hydrogen sulfide pyrolysis in the temperature range of 800-1100 °C. They acquired kinetic data on the thermal dissociation of hydrogen sulfide diluted in argon 95% by volume in the absence of elemental sulfur as well as in the presence of elemental sulfur to take into account the auto acceleration of hydrogen sulfide pyrolysis that has been observed experimentally. The type of the reactor used in their investigation was a continuous perfectly mixed quartz reactor to avoid any catalytic effect on the decomposition of the hydrogen sulfide stream. This type of reactor was proposed by David and Matras [68]. The investigators noted that the pyrolysis of hydrogen sulfide to produce hydrogen and sulfur is subjected to equilibrium limitation and this equilibrium limit can be reached in a few seconds above 1000 °C (42% at 1000°C for a dilute 5% H_2S stream, according to Binoist and co-workers [67]). They, like most other studies, targeted the range of residence times from 0.4 to 1.6 seconds. They also conducted experiments at lower temperatures of 600 and 700 °C. These experiments showed no decomposition of hydrogen sulfide which indicated that there was no pyrolysis of hydrogen sulfide taking place at temperatures

up to 800 °C for residence times of 1.5 second. Experiments carried out in the presence of added elemental sulfur showed that the conversion rate accelerates and the equilibrium limit is achieved at temperatures lower than 1000 °C in few seconds.

Table 2. Detailed radical mechanism of hydrogen sulfide thermal pyrolysis [Binoist et al. [67]].

	A ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	n	E ($\text{cal} \cdot \text{mol}^{-1}$)	no.
$\text{H}_2\text{S} + \text{M} = \text{H} + \text{SH} + \text{M}$	1.76×10^{15}	0.0	66 200	R1
$\text{H}_2\text{S} + \text{M} = \text{H}_2 + \text{S} + \text{M}$	2.39×10^{15}	0.0	60 250	R2
$\text{H} + \text{SH} = \text{H}_2 + \text{S}$	1.29×10^{13}	0.0	7210	R3
reverse	2.70×10^{14}	0.0	21 030	R-3
$\text{H} + \text{H}_2\text{S} = \text{H}_2 + \text{SH}$	2.90×10^{14}	0.0	13 000	R4
reverse	1.18×10^{14}	0.0	27 100	R-4
$\text{H}_2\text{S} + \text{S} + \text{M} = \text{H}_2\text{S}_2 + \text{M}$	3.60×10^{12}	0.0	0.0	R5
reverse	3.00×10^{20}	-1.0	52 800	R-5
$\text{SH} + \text{H}_2\text{S}_2 = \text{H}_2\text{S} + \text{HS}_2$	5.20×10^{14}	0.0	6100	R6
reverse	6.80×10^{14}	0.0	29 700	R-6
$\text{SH} + \text{HS}_2 = \text{H}_2\text{S} + \text{S}_2$	2.00×10^{13}	0.0	4700	R7
reverse	4.80×10^{13}	0.0	38 400	R-7
$\text{SH} + \text{S} + \text{M} = \text{HS}_2 + \text{M}$	6.00×10^{11}	0.0	0.0	R8
reverse	6.00×10^{12}	0.0	70 900	R-8
$\text{H} + \text{S}_2 + \text{M} = \text{HS}_2 + \text{M}$	1.00×10^{18}	0.0	1510	R9
reverse	1.00×10^{17}	0.0	31 070	R-9
$\text{SH} + \text{S} = \text{H} + \text{S}_2$	8.97×10^{15}	0.0	15 000	R10
reverse	6.98×10^{16}	0.0	31 300	R-10
$\text{SH} + \text{SH} + \text{M} = \text{H}_2\text{S}_2 + \text{M}$	3.20×10^{13}	0.0	0.0	R11
reverse	2.70×10^{22}	-1.0	58 600	R-11
$\text{SH} + \text{S}_2 = \text{S} + \text{HS}_2$	1.40×10^{12}	0.0	33 700	R12
$\text{H}_2\text{S}_2 + \text{M} = \text{H} + \text{HS}_2 + \text{M}$	9.10×10^{19}	-1.0	70 200	R13
$\text{H}_2\text{S} + \text{S} = \text{H} + \text{HS}_2$	1.80×10^{13}	0.0	25 800	R14
$\text{SH} + \text{SH} = \text{H}_2\text{S} + \text{S}$	0.75×10^8	1.14	100	R15
reverse	2.29×10^8	1.30	17 100	R-15
$\text{S} + \text{S} + \text{M} = \text{S}_2 + \text{M}$	1.00×10^{15}	0.0	0.0	R16
$\text{HS}_2 + \text{HS}_2 = \text{H}_2\text{S}_2 + \text{S}_2$	6.00×10^{12}	0.0	9100	R17
$\text{H}_2\text{S}_2 + \text{H} = \text{H}_2\text{S} + \text{SH}$	6.00×10^{12}	0.0	5200	R18
$\text{H} + \text{HS}_2 = \text{H}_2\text{S} + \text{S}$	6.00×10^{13}	0.0	8400	R19
$\text{H} + \text{HS}_2 = \text{H}_2 + \text{S}_2$	4.30×10^{13}	0.0	1400	R20
reverse	4.72×10^{13}	0.0	57 610	R-20
$\text{SH} + \text{M} = \text{S} + \text{H} + \text{M}$	6.00×10^{12}	0.0	73 600	R21
reverse	3.60×10^{15}	0.0	9300	R-21
$\text{S} + \text{H}_2\text{S}_2 = \text{SH} + \text{HS}_2$	6.00×10^{12}	0.0	8200	R22

A complementary study was conducted to investigate if the alumina has an effect on the reaction as compared to the quartz. The experiments for both materials

were carried out at temperatures of 1100°C and 1200°C. The results of this study conclude that the conversion in alumina reactor is always higher than that in quartz system. This consistently higher conversion of hydrogen sulfide in alumina reactor ensures that the alumina walls have catalytic effects on the H₂S pyrolysis and is unsuitable for the study of the homogeneous reaction of H₂S pyrolysis. They used a detailed reaction mechanism to carry out numerical simulations and compared the numerical results with experimental data. The detailed radical mechanism is shown in

Manenti et al. [69] proposed detailed kinetic mechanism for pyrolysis and oxidation of sulfur compounds that accounted for the presence of light hydrocarbons, ammonia and other species that are often present in acid gases. This mechanism was successfully validated against data available in the literature and industrial data acquired from different Claus plants. The detailed kinetic model for sulfur recovery units they proposed was on the principles of hierarchy, generality, and modularity as for the previous kinetic models already developed for pyrolysis and combustion of hydrocarbons and biomasses (Ranzi et al. [70]). The sulfur subset derives from the work of Glarborg's group (Rasmussen et al. [71]), which is adapted to the typical operating conditions of sulfur recovery units, was focused on improving the agreement with experimental/industrial data. It should be noted that the kinetic scheme differs from that of other literature schemes since its kinetic parameters accounts for the presence of light hydrocarbons, ammonia, and other species usually present in the feedstock of industrial sulfur recovery units. They have applied the revised kinetic model to several industrial cases with good agreement with respect to the industrial data. The experimental data that they have considered for the pyrolysis model

validation was acquired from Binoist et al. [67]. The trends of their results show that the model is in a good agreement with the experimental data when no sulfur is fed to the system. On the other hand, when the sulfur was fed the data are systematically underestimated. Therefore, the model can only be used when no sulfur is fed to the system. For this reason, a coupled sensitivity and local reaction fluxes analysis was performed and led to the identification of a few reactions whose parameters can be adjusted in order to get better data fitting. These minor adjustments are possible if considering the range of uncertainty about the kinetic parameters. The kinetic model prevision is improved by 10-20%, depending on the operating temperature. In order to simulate COS formation, they [69] considered Karan's data [72] and reactor configuration. They found a better agreement between data and their model using revised kinetic parameters at temperatures higher than 1000°C. Such temperatures would be of less interest for the Claus process, but for the pyrolysis, this must be taken into account.

Cong et al. [73] examined numerically production of H_2 via the thermolysis of H_2S for direct hydrogen and sulfur production as well as oxidation of H_2S . They proposed a detailed reaction mechanism that captures the chemistry involved in its high temperature decomposition. The simulation results obtained using the proposed mechanism is compared with a wide range of experimental data from different types of reactors that include plug flow and stirred reactors, premixed laminar flames, and shock tubes, and a satisfactory agreement between them is found. Significant improvements in model predictions are obtained with the proposed mechanism when compared to previously published mechanism. After its validation, the mechanism was then used to

investigate the major reactions involved in hydrogen production. They also investigated production of H₂ via partial oxidation of H₂S under adiabatic conditions using their validated mechanism.

2.3. Reformation of Hydrogen Sulfide in Presence of Impurities

Most of the previously mentioned research have examined the thermal decomposition reaction of hydrogen sulfide stream. Practically, hydrogen sulfide separated out from crude oil and gas wells has many contaminants such as: carbon dioxide, nitrogen, ammonia, methane, carbonyl sulfide, carbon disulfide, benzene, toluene, xylene (commonly referred to as BTX). Each of these impurities affects the thermal decomposition reaction differently. Hydrogen-constituted impurities, such as ammonia and hydrocarbons, in hydrogen sulfide stream enrich its hydrogen feedstock and are expected to enhance hydrogen production from hydrogen sulfide pyrolysis.

Investigations on reaction between hydrogen sulfide and hydrocarbons have been known for more than 80 years. Traditionally, these investigations started with reaction between hydrogen sulfide and methane. However, studies on reaction between hydrogen sulfide and methane were not envisioned for hydrogen production. One of the earliest studies on reaction between hydrogen sulfide and methane was by Waterman and Van Vlodrop [74] who conducted experiments in a tubular quartz reactor over a temperature range of 1080-1280 °C at residence time of 0.4-0.7 second to primarily produce carbon disulfide via the following reaction:



Erekson [75] used hydrogen sulfide in a chemical cycle with methane to produce gasoline via the following reactions:



Although hydrogen sulfide and methane was the initial step to produce the reactants of the second step, which can be considered the main step for production of gasoline, neither destruction of hydrogen sulfide nor hydrogen production was the focus of their study. Hydrogen and hydrogen sulfide were only the intermediate products.

The interest in exploitation of this reaction for enhanced production of hydrogen from reformation of hydrogen sulfide in the presence of methane has grown in recent times. Thermodynamics assessment of hydrogen production via thermal dissociation of a mixture of hydrogen sulfide and methane using equilibrium calculations, conducted by Huang and T-Raissi [76, 77], identified conditions to eliminate carbon deposits. Another thermodynamic study supported by experimental work was done by Megalofonous and Pappayanakos [78]. They studied production of hydrogen from hydrogen sulfide and methane mixture over relatively low temperatures of 713-860 °C. This temperature range was not high enough for significant hydrogen production from homogeneous reaction, so they used molybdenum disulfide to accelerate the reaction and reach equilibrium composition of products at such relatively low temperature range.

Karan and Behie [79] examined the pyrolysis of hydrogens sulfide in presence of methane in order to improve the understanding of the kinetics of CS₂ formation. They used a high temperature quartz flow reactor with pressures of 101-150 kPa in temperature range of 800- 1250 °C and residence time of 90-1400 ms. They also studied

the kinetics of sulfur and methane under the same conditions. They found that the reaction between sulfur and methane is very rapid to form CS_2 and H_2S . They also found that H_2S decomposition is the rate limiting step for CS_2 formation. However, the conversion of H_2S increased in the presence of methane, they inferred that consumption of H_2S proceeds at a characteristic rate independent of any reaction of H_2S with methane. They observed higher rates of formation of CS_2 in the reaction with sulfur rather than reaction with hydrogen sulfide. They also observed higher consumption of hydrogen sulfide and consequently higher production of hydrogen because of consuming sulfur to form CS_2 which shifts equilibrium towards more consumption of H_2S .

Towler and lynn [80] studied the thermochemistry and reaction kinetics of mixtures of H_2S and CO_2 . When hydrogen sulfide is heated above 600°C in the presence of carbon dioxide, the conversion of H_2S to elemental sulfur is greater than when hydrogen sulfide is heated alone. Formation of elemental sulfur is favored by high temperature, low pressure, and low water content in the gas. The rate-limiting step is the thermal dissociation of H_2S . The hydrogen then equilibrates rapidly with CO_2 , forming CO and H_2O via the water-gas-shift reaction. The equilibrium of H_2S dissociation is therefore shifted to favor the formation of elemental sulfur. The main byproduct is COS , which is formed by a reaction between CO_2 and H_2S that is analogous to the water-gas-shift reaction. A quench rate of 1000°C/s or greater is sufficient to prevent loss of elemental sulfur by back-reaction or reaction to COS during cooling. Formation of small amounts of SO_2 and CS_2 is thermodynamically feasible but has not been observed. A process based on this chemistry has significant advantages over the Claus process in that it need

not produce any tail gas, it allows recovery of the chemical (or fuel) value of the hydrogen from the H₂S, and it requires much less stringent process control.

Karan et al. [72, 81, 82] studied the homogeneous gas phase COS reactions experimentally and numerically to find the key reaction to form this compound. They conducted three sets of experiments in tubular reactor over a temperature range of 800-1200°C at pressure of 120-160 kPa. The three sets of experiments were conducted with three different diluted mixture (98% dilution): CO₂/sulfur, CO₂/H₂S and CO/H₂S. The corresponding gas residence time ranged from 0.5 to 2.0 s. Experimental results showed no formation of COS in detectable concentration from CO₂/sulfur mixture. Also, negligible amount of COS was formed from reactions of CO₂ with H₂S, contrary to popular belief. They found that hydrogen sulfide decomposition into hydrogen and sulfur plays a critical role in the formation of CO and COS where hydrogen produced from H₂S decomposition reacts with CO₂ to form CO. At higher temperatures, the pyrolysis of H₂S becomes relevant: the production of S₂ leads to COS (reaction 9).



Otherwise, at low temperatures (<900°C) according to the molecular reaction between CO and H₂S (reaction 10):



They also described these reactions by the simple rate expression: $r_{H_2S} = k_1 C_{H_2S} C_M$, where C_M is the molar concentration of the collisional molecule (N₂) and the rate constant $k_1 = (1.68 \pm 0.86) \times 10^{11} \exp \left[-\frac{2,8940 \pm 840 \text{ K}}{T} \right] m^3/[kmol.s]$. Further, the reaction of CO with H₂S was found to be rapid and equilibrium COS conversions were attained in less than 700 ms at temperatures greater than 1000°C. The

COS forming reaction between CO and H₂S could be represented by the rate expression

$r_{COS} = k_3 C_{CO} C_{H_2S}^{0.5}$, where the rate constant $k_3 = 1.59 \pm 0.86] \times 10^5 \exp \left[\frac{-13340 \pm 930 K}{T} \right] \left[\left(\frac{m3}{kmol} \right)^{0.5} / s \right]$. In a (CO₂+H₂S) mixture, the. Finally, the rate of CO formation could be described by the following rate expression: $r_{CO} =$

$$k_4 C_{CO_2} C_{H_2}^{0.5}, \text{ where } k_4 = (3.95 \pm 0.35) \times 10^{10} \exp \left[\frac{31220 \pm 180 K}{T} \right] \left[\left(\frac{m3}{kmol} \right)^{0.5} / s \right].$$

Steam reformation of hydrogen sulfide has also been studied by AuYeung and Yokochi [83]. Steam reformation of hydrogen sulfide is highly endothermic since it has a positive Gibbs free energy change. The steam reformation of hydrogen sulfide was investigated under favorable circumstances (excessive dilution with steam and inert carrier) over a variety of catalytic (using molybdenum disulfide) as well as non-catalytic settings in a quartz tube. Successful results were obtained by pretreating a molybdenum wire with H₂S at high temperature. They determined apparent Arrhenius parameters for both thermal splitting and steam reformation of hydrogen sulfide.

Another study on steam reformation of hydrogen sulfide mixed with methane with an objective of hydrogen production has been done by Sadooghi and Rauch [84]. They studied experimentally and numerically the steam reformation of a mixture of methane and different amounts of hydrogen sulfide in the feed stream. They developed a two dimensional pseudo heterogeneous model to simulate methane steam reforming reactions in a packed bed tubular reactor based on mole and energy balance equations for the catalyst and the fluid phases. Negative effects of sulfur on reforming process has been highlighted. A parametric study was done including effects of different steam to carbon ratios, space velocities, temperatures and different amount of sulfur on

methane conversion and temperature distribution within the reactor. The results were verified against the experimental results.

Dokiya et al. [85] studied a two-step decomposition of hydrogen sulfide with carbon monoxide following the reactions shown below:



They could produce an equilibrium amount of hydrogen via the first reaction (ca. 40%, 200°C, 1 atm. CO/H₂S=2.2) with a cobalt sulfide or nickel sulfide catalyst. They could also recover an almost equilibrium amount of carbon monoxide and elemental sulfur from carbonyl sulfide non-catalytic decomposition at 830°C under 1 atm. with a sufficient reaction time. Carbon dioxide was formed as a by-product in the second reaction, however, its yield was only 5% of the carbon monoxide produced. Also, the recombination of carbon monoxide with elemental sulfur recovered cannot be neglected. Thus, rapid separation of sulfur from carbon monoxide is required. From these results, they inferred the potential of this two-step thermochemical cycle that can produce more hydrogen than that produced by direct decomposition of hydrogen sulfide.

The combustion of acid gas, specifically in presence of carbonaceous impurities, is expected to generate some unwanted by-products such as COS, CS₂, SO₂ and other sulfurous compounds. COS and other undesired compounds are produced in the reactor due to the interaction of hydrocarbons and sulfur compounds. They are unwanted compounds because they limit sulfur recovery and poison certain catalysts.

2.4. Thermal Decomposition of Hydrogen Sulfide with Equilibrium Shift

Other researchers investigated shifting the equilibrium limit on the conversion of hydrogen sulfide by removal of one of the products either hydrogen or sulfur. Different methods were utilized for removal of one of the products such as: condensation of sulfur and using membranes for removing hydrogen.

Fukuda et al. [57] studied the decomposition of hydrogen sulfide on molybdenum disulfide and tungsten disulfide catalyst at 500 - 800°C in a closed circulating system. They found that molybdenum disulfide decomposes hydrogen sulfide effectively into hydrogen and sulfur over the whole range of temperature. They also were able to shift the equilibrium limit by continuous removal of sulfur and intermittent separation of hydrogen from the reaction gas mixture at 800°C to achieve conversion of hydrogen sulfide that exceeds 95%.

Sugioka and Aomura [86] studied the catalytic decomposition of hydrogen sulfide over molybdenum disulfide in a closed circulation system at 500°C similar to Fukuda [57]. The catalytic activity of MoS₂ was remarkably enhanced by reduction with hydrogen but was not considerably increasing the evacuation temperature. A possible mechanism was proposed for the catalytic decomposition of hydrogen sulfide over MoS₂ where the coordinative unsaturation site of MoS₂ surface formed by reduction with hydrogen acts as the active site.

Although it was easier to remove sulfur rather than hydrogen, researchers also worked on removal of hydrogen produced from hydrogen sulfide decomposition using membranes.

Kameyama et al. [87] investigated the possibilities of using microporous ceramic membranes in a reactor for production of hydrogen from hydrogen sulfide. A microporous vycor-type glass tubing membrane of a mean pore diameter of 45\AA and new microporous alumina tubing membrane of diameter 1020\AA could be used up to 800°C and at higher temperatures, respectively, a membrane for separating hydrogen and hydrogen sulfide. The microporous alumina tubing membrane has a 30-fold higher permeability than the microporous vycor glass tubing membrane. When these membranes were applied to the direct decomposition of hydrogen sulfide, the yield of hydrogen increased by about two times the equilibrium yield calculated for the process without hydrogen removal.

Edlund and Pledger [88, 89, 90] investigated the application of platinum-based hydrogen-permeable composite-metal membrane for removal of hydrogen during environmentally clean thermolysis of hydrogen sulfide. Vanadium was used as the base metal since it does not suffer from hydrogen embrittlement and has good permeability for hydrogen. Platinum was used on the feed side to protect the vanadium from attack of hydrogen sulfide since the platinum layer resists irreversible chemical attack by H_2S at 700°C and partial pressures of up to 115 psi. Therefore, the membrane contains a platinum coating layer on the feed side of the membrane. Removal of hydrogen during thermolysis of hydrogen sulfide resulted in higher conversions than can normally be obtained due to achieved equilibrium shift. The detailed procedure of preparing the composite membrane has been discussed. This membrane has been used in a laboratory-scale membrane reactor to drive the decomposition of H_2S to greater than 99.4% of complete conversion for production of hydrogen and sulfur. Experimental

results with respect to performance and the determination of the rate-limiting step for the thermolysis of hydrogen sulfide in the membrane reactor were reported and discussed. The thermal decomposition of H_2S within the membrane reactor was accurately described by a simple model that considers the initial composition of the feed gas, the equilibrium expression for H_2S decomposition and the hydrogen flux for the membrane.

Another method that has been exploited to shift the equilibrium towards higher conversion of hydrogen sulfide by continuous removal of one of the products was thermal diffusion. The sulfur formed condenses on the cold surface of the column and hydrogen moves preferentially to the top of the column. Nishizawa et al. [91] used thermal diffusion column have a length of 1m and an external diameter of 0.012m silica pipe for hot wall and surrounded by a pyrex glass tube of internal diameter 0.024m and a pyrex glass jacket of internal diameter 0.032m . The hot wall temperature was taken as the mean of temperatures measured at five different positions by means of thermocouples. The cold wall was supplied with tap water with inlet and outlet temperatures in the ranges 288-293K and 293-298K, respectively. Three columns having differences in the spacing between the hot and cold surfaces, total volume and the mode of heating were tested. It was found that a mixture of 35-40% hydrogen in hydrogen sulfide separated to 88-92% hydrogen at the top of the column in 30 min. It was also shown that there was no decomposition of H_2S at this temperature in the absence of catalyst. The hot surface was coated with catalysts and the performance of the thermal diffusion columns for the decomposition of H_2S was investigated at 773K. The condensation of sulfur on the cold surface and the preferential transport of

hydrogen up the column caused the decomposition reaction to continue beyond equilibrium value.

Our research team has reported on reactor conditions under which COS, SO₂, CS₂ and other sulfur compounds are produced in context of Claus reactor process [92, 93, 94, 95, 19]. Most importantly, we have revealed the increased potential of H₂ production from acid gases containing benzene, toluene and xylene (BTX) [96, 97, 98, 99]. These are common aromatic impurities often found in acid gases. It is important to examine the reactor conditions under which hydrogen production can be maximized while minimize the formation of unwanted sulfurous compounds.

2.5.Catalyst Role in Hydrogen Sulfide Thermal Pyrolysis

Due to the high endothermic nature of the reaction and high temperature required to decompose hydrogen sulfide to produce hydrogen and sulfur, efforts have been made to develop catalysts to reduce the thermal energy required for decomposing the hydrogen sulfide so that lower temperatures are required for the pyrolysis.

Binoist et al. [67] showed that alumina has a catalytic effect on the H₂S pyrolysis reaction compared to quartz which has no or minimal catalytic effect. Experiments showed that conversion in alumina reactor is consistently higher than that in quartz reactor which substantiate the catalytic effect of the alumina walls on the thermal pyrolysis of hydrogen sulfide.

The thermal cracking of hydrogen sulfide has also been studied catalytically using molybdenum disulfide (MoS₂) as a catalyst. The catalytic activity of MoS₂ decreased with time, stabilizing at 65% of the initial value [57]. Fakuda et al. [57]found that the catalytic effect of molybdenum disulfide on the thermal splitting of hydrogen

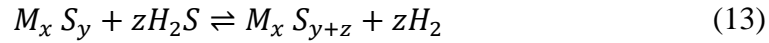
sulfide to hydrogen and elemental sulfur is effective over the temperature range of 773-1073 K. They also investigated the catalytic effect of tungsten disulfide, WS_2 . However, it has been found that the catalytic activity of Molybdenum disulfide is higher than tungsten disulfide [57].

Yumura and Furimsky [100] tested manganese nodule as a potential adsorbent for H_2S removal. In the first stage the H_2S was removed via its reaction with the adsorbent, after the complete sulfurization, the adsorbent had catalytic effects on H_2S decomposition. In the temperature range of 600°C to 800°C the amount of H_2S which reacted with one gram of the nodule per unit time was temperature independent whereas H_2S showed a fivefold increase in the decomposition. The rate of H_2S reaction with the adsorbent was of first order while H_2S decomposition was of a half order.

They also tried the addition of 10 wt% of CaO to the manganese nodule and results showed that it had little effect on slope of H_2S adsorbed/g of nodule versus time and H_2S decomposed/g of nodule versus time correlations but increased the sulfur capacity of the adsorbent by about 30%.

Bishara et al. [53, 101] studied the decomposition of hydrogen sulfide into hydrogen and sulfur using concentrated solar radiation. The effect of temperature and residence time on hydrogen yield was studied using alumina, nickel-molybdenum sulfide, and cobalt-molybdenum sulfide as catalysts. It was found that hydrogen yield of 13-14% can be obtained in a very short residence time (0.3s) and at temperatures less than 800°C. The decomposition mechanism followed a second-order irreversible rate equation.

In analogy to Molybdenum disulfide and tungsten disulfide, Chivers et al. [102, 58] investigated the effect of different metal sulfides on hydrogen evolution from hydrogen sulfide stream. They studied the sulfides of Vanadium, Iron, Copper, Chrome and Zinc over a temperature range of 673-1073 K. The results of different metal sulfides were compared to Molybdenum disulfide. It was found that catalysts containing Fe_7S_8 could achieve higher conversion. It was revealed that for the series Cr_2S_3 , MoS_2 and WS_2 , MoS_2 is the most active catalyst at temperature higher than 873 K but for lower temperature Cr_2S_3 and WS_2 produced higher yield of hydrogen. They also suggested a two-stage process to represent the hydrogen sulfide decomposition in the presence of metal sulfide as a catalyst, as follows: (reactions 13-15)



In the first stage, the lowest metal sulfide $M_x S_y$ interacts with hydrogen sulfide, forming higher metal sulfide $M_x S_{y+z}$ and hydrogen. The lower metal sulfide is regenerated from the higher metal sulfide by forming elemental sulfur.

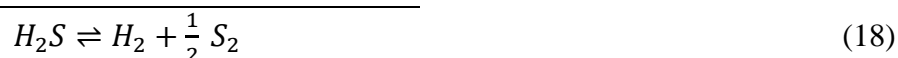
Other sulfides have also been reported in the literature that includes nickel sulfide and cobalt sulfide [20].

It has been shown that metal oxides have catalytic effect as well. Metal oxides participate in the thermal pyrolysis of hydrogen sulfide through a two-stage process, as proposed by Al-Shamma et al [51].

The first stage is the formation of metal sulfide from the reaction of hydrogen sulfide and metal oxide. In the second stage the metal sulfide film on the surface of the

metal oxide plays the role of a catalyst through the two-stage process proposed by Chivers et al. [102, 58]. The metal sulfide reacts with the hydrogen sulfide stream forming higher metal sulfide. The lower metal sulfide is regenerated from the higher sulfide by forming elemental sulfur.

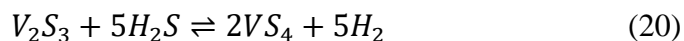
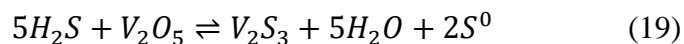
Kiuchi et al. [103] proposed another two-step thermochemical cycle shown below following the same pattern of transition metal sulfides discussed earlier and experimental studies were made on the cycle.



In the case where Ni_3S_2 alone was used without inert additions, nickel sulfide sintered or partly fused due to the melting point depression resulting from the thermal decomposition of formed NiS . They suggested preventing such sintering by mixing the nickel sulfide powders with Al_2O_3 or MoS_2 . The cyclic reactions were thereby shown to provide a stationary high decomposition rate of H_2S . This research showed that the use of lower sulfides such as Ni_3S_2 , may be regarded as rather promising based on the thermodynamic investigation of the respective reactions composing the cycle [103]. The comparison between the sulfurization reactions of NiS to NiS_2 and of Ni_3S_2 to NiS further showed that the latter was superior to the former with respect to the kinetics and thermodynamical properties of the reaction [103].

Al-Shamma et al. [51, 104] studied the V_2O_5 /alumina in the reaction of H_2S decomposition over temperature range of 773-873 K and explained the reaction in the two-stage process as given before.

The thermal pyrolysis of hydrogen sulfide in the presence of V₂O₅/alumina is as follows [reactions 19-21]:



Note that iron oxide, is known to be easily sulfidized to iron sulfide that exhibits catalytic activity in the thermal pyrolysis of hydrogen sulfide. Reshetenko et al. [105] investigated the catalytic effect of metal oxides. They studied the effect of Fe₂O₃ and V₂O₅ over the temperature range 773-1073 K. They measured the kinetic parameters of catalytic hydrogen sulfide cracking in the presence of catalysts Fe₂O₃ and V₂O₅.

2.6.Summary

A literature review conducted on the non-catalytic thermal decomposition of hydrogen sulfide gas to hydrogen fuel. Most studies have focused on the kinetics of thermal decomposition of hydrogen sulfide into hydrogen and sulfur and reported various kinetic parameters. These studies have shown that thermal pyrolysis of hydrogen sulfide is equilibrium limited, thus high reactor temperatures (above 1300 °C) are required for the feasibility of hydrogen production. A review of the available literature revealed that kinetic parameters varies significantly and thus do not provide a unified description of the reaction kinetics of hydrogen production from hydrogen sulfide despite the wide available information. A few attempts have also been made to develop a detailed reaction mechanism for hydrogen sulfide pyrolysis under low and high temperature conditions. However, these mechanisms require more rigorous validations and optimizations under high temperature conditions (>1373K) and such

experimental data are very scarce in the open literature. It is recommended that the well-studied mechanisms of hydrogen sulfide oxidation be combined with a detailed pyrolysis mechanism. Such a combined mechanism will favor prediction of pyrolysis and oxidation reactions which are favorable during acid gas (H_2S and CO_2) pyrolysis to produce hydrogen and elemental sulfur. This will allow further feasibility studies to determine the optimum reactor conditions to achieve hydrogen production and clean sulfur recovery from hydrogen sulfide.

Practically, hydrogen sulfide stream has many impurities including hydrocarbons and ammonia, these hydrogen constituted species enrich the hydrogen feedstock in hydrogen sulfide. However, most studies on pyrolysis of hydrogen sulfide have focused on thermal decomposition of hydrogen sulfide only. Production of hydrogen from a stream of hydrogen sulfide having these impurities has not been the primary focus of these studies. The high temperature required for the thermal pyrolysis of hydrogen sulfide possibly acts as inhibiting factor to make this process economical. Therefore, production of hydrogen via partial oxidation of hydrogen sulfide under ultra-fuel rich conditions is a step towards making this process auto-thermal.

Chapter 3: Experimental Facility

In this Chapter, we discuss details of the experimental facility, diagnostics and procedures that have been used throughout the course of this study.

3.1. Experimental Setup

The experimental facility was designed to facilitate the understanding of the detailed chemistry of hydrogen sulfide pyrolysis in a laboratory-scale reactor. The geometry and configuration of the experimental setup was designed to provide defined and well controlled experimental conditions. The experimental set-up will also favor the examination of wide range of residence time, temperature, wide range of hydrogen sulfide concentrations and other input operational conditions that are suitable for the understanding of the detailed process chemistry and sulfur conversion while ensuring safe operation in the laboratory vicinity. It also offers the flexibility to examine the effect of catalysts, acid gas impurities, such as methane, ammonia and carbon dioxide benzene, toluene, xylene. Detailed description of the experimental setup is given below. A schematic diagram of the experimental setup is shown in Figure 2. The experimental setup consisted of four sections: gas supply manifold, thermal reactor, sampling and quenching and gas analysis.

3.1.1. Thermal Reactor (Quartz Tube Reactor)

The main component of the experimental facility was basically a quartz tube reactor section. Quartz was chosen as the reactor material for two reasons. First, quartz has superior thermal stability at high elevated temperature up to 1700 K. Second, quartz, unlike other materials that can withstand high temperatures such as alumina, has been shown not to have any catalytic effect on H_2S decomposition [48, 67] and

hydrocarbons decomposition and consequently no effect on the decomposition of H_2S alone or decomposition of a mixture of H_2S with impurities [79]. In addition, protracted use of quartz reactor revealed no noticeable effects on its inner surface from the pyrolysis of acid gas, divulging that quartz has no catalytic effect on acid gas pyrolysis.

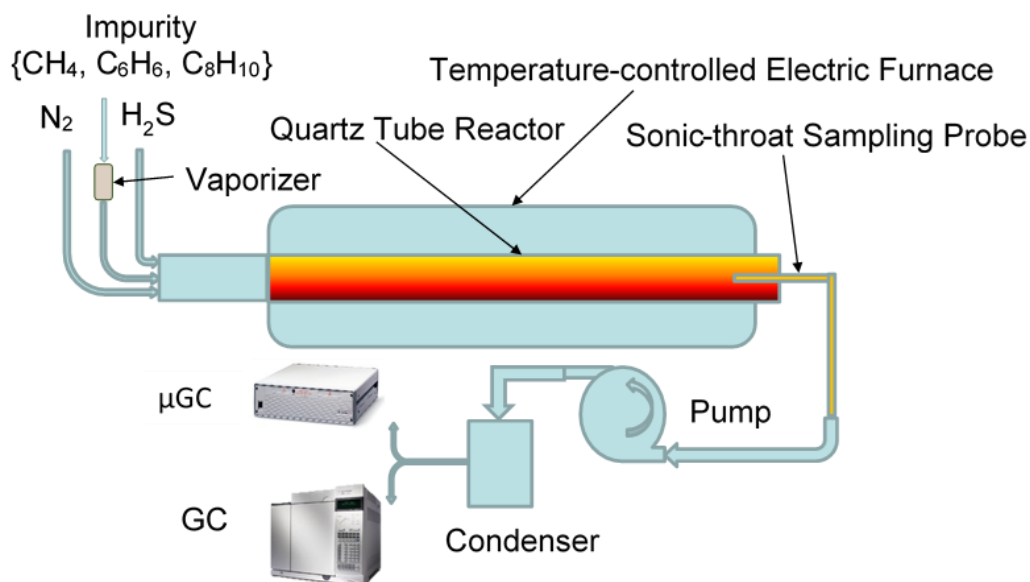


Figure 2. A schematic diagram of the experimental setup

Different quartz tubes with different diameter has been used at the beginning of this research. Then, an optimization on this important parameter in reactor design has been made. The size of the reactor has been affected by three factors: 1) Length of the heated cavity inside the furnace housing the reactor. 2) Range of flow rates that can be supplied to the reactor so that the desired range of residence time can be provided. 3) Ratio between the diameter and length is high enough to preheat the gases quickly at relatively low flow rates. A reactor of 0.006m diameter has been selected that provides 0.36m total length having 0.3m length heated reaction zone. The quartz reactor has been accommodated inside an electrically heated-temperature controlled horizontal

tubular furnace. The furnace had a temperature controller that kept a defined and uniform temperature throughout the furnace cavity with operating temperatures of up to 1773K. The high temperature range of the furnace will be useful in the experiments with quartz tube where non-catalytic reaction is examined. Lower operating temperature range can be utilized in examining catalytic pyrolysis of hydrogen sulfide.

3.1.2. Gas Supply Manifold and Control System

Thermal flow controllers connected to gas cylinders of high purity gases to supply the required flow rate of H_2S , CH_4 and N_2 controlled the metered gases supplied to the reactor. Based on the size of the reactor, the flow rates of each gas as well as total flow rate of the gases were calculated to have the residence time range of interest. Controlling the flow rate of each gas provided control on the desired inlet composition into the reactor, while controlling the total flow rate of the gases provided control on residence time of the gases inside the reactor. The effect of heating of the gases from room temperature to furnace temperature on the flow velocity has been taken into consideration. The targeted range or residence time was determined based on the data in the literature that provided the residence time required to reach the steady state at relatively high temperature. The purpose of the variation of residence time was to study the evolutionary behavior of hydrogen as well as consumption of hydrogen sulfide and other reactants that can be used in the validation of the developed numerical models as well.

In case that the impurity injected with hydrogen sulfide is normally liquid at room temperature such as benzene, toluene and xylene, thermal flow controllers were still used to supply the gaseous phase reactants while different setup was used to meter

liquid reactants, vaporize them and mix them with other gaseous phase reactants prior to injection into the reactor. A liquid handling pump was used to supply the liquid impurity into a heated vaporizer which can operate up to 493 K prior to mixing with metered flow of hydrogen sulfide and nitrogen stream that provided controlled and desired mixture composition at entrance to the reactor. Liquid and gaseous flow rates of BTX were calculated based on their density. The targeted residence time was still achieved by controlling the total flow rate of all species. The calculated total flow rate to achieve the targeted residence time was then divided between the reacting species constituting the inlet stream according to the desired composition. Therefore, the flow rate of each component determine the composition of the inlet stream and the total flow rate of the reacting components determined the residence time of the reactants inside the reactor. First, nitrogen was injected into the reactor to ensure no residual gas was present. Hydrogen sulfide flow was allowed to mix with the nitrogen flow prior to mixing with BTX vapors before their entrance in to the reactor.

It can be noticed that controlling the flow is crucial in our study to accurately supply the required flow rate and not only the residence time of the reactants inside the reactor but also the composition of the reacting stream. That is why different flow controllers with different ranges of flow delivery rates should be used accordingly to minimize error. The thermal flow controllers can deliver flows with the least possible error of $\pm 1\%$.

In almost all experimental runs throughout this research, the main reactants stream was diluted in nitrogen. Nitrogen was chosen as diluent since it is inert to thermal decomposition reaction. The dilution was kept as high as 90% or higher. This

high dilution was meant to serve two purposes. First, the relatively high thermal capacity of nitrogen helps in keeping the temperature of the gases inside the reactor constant from the possible damping by the endothermicity nature of the decomposition reaction. This assures maintaining near isothermal operation of the reactor. The other purpose is related to the safe operation of the facility. Since the reactants stream has one of its components or more being either toxic, corrosive or flammable, diluting this reactants with inert diluent without affecting the reaction helps in reducing the amounts of reactants utilized during the experiment. This reduction in the amounts of reactants utilized contributes in safer operation of the facility by limiting sulfurous compounds consumed/formed in the reactor as well as the remaining non-decomposed reactants.

3.1.3. Sampling System.

Gaseous products at exit of the reactor were collected for analysis using an air-cooled quartz sonic-throat sampling probe with a fine tip (0.2 mm inner diameter) that was positioned at longitudinal centerline axis of the reactor. The fine tip allows gas sampling with negligible disturbance to the flow. The sampling probe quenched the reaction to prevent any occurrence of reverse reactions between the high temperature products by rapid decrease in temperature. Accelerating the sampled stream significantly along the fine tip passage of the probe causes rapid expansion (decrease in pressure) of the flow that is accompanied by rapid decrease in

temperature. The air flow induced by the fume hood inside which the entire facility is accommodated helps in cooling the collected sample significantly faster. Liquid and solid sulfur was observed in the sampling probe indicating lowering the temperature significantly to quench the reaction. A peristaltic pump was used for suction of the quenched sampled products stream from outlet of the reactor and injected it into a condenser. The purpose of the condenser is to condense any remaining sulfur vapors as well as any condensable vapors to ensure that only gaseous products were flowing.

The pump was able to provide flow rates in the range of 0.3 up to 6 liter/min.

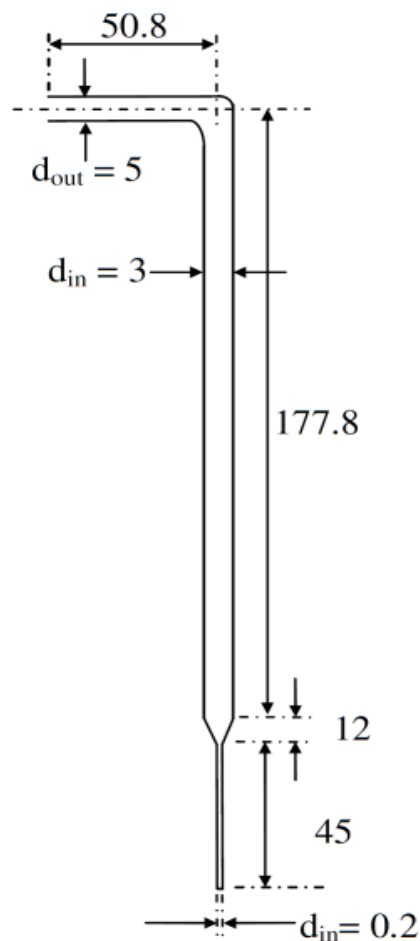


Figure 3. Schematic diagram of the sampling probe, dimensions are in millimeter.

3.2.Diagnostics:

3.2.1. Gas Chromatography:

The analysis of the gas products stream was conducted using a gas chromatograph (GC). After the condenser and removing any condensable gases to ensure proper functionality of the GC, sampled gases were injected online into the GC. Three different detectors were used in two different GCs; one was Agilent 3000 micro-GC which had four channels equipped with thermal conductivity detectors (TCD). The

other GC was Agilent model 7890A GC system equipped with two different detectors: flame ionization detector (FID) and flame photometric detector (FPD). Thermal conductivity detector (TCD) was used to measure composition of H_2 , N_2 , CO , CO_2 and CH_4 . Flame photometric detector (FPD) provided the composition of stable sulfurous compounds (e.g. H_2S , CS_2 , SO_2 , COS). A flame ionization detector (FID) indicated presence of any hydrocarbon vapors to provide the concentration of gaseous hydrocarbons (e.g. CH_4 , C_6H_6 , C_8H_{10} ...).

3.3. Thermal Characterization of the Reactor

In order to achieve well-defined conditions, it is desirable that the temperature be isothermal. Since perfect isothermality is not practically possible, operating the reactor as close as possible to isothermal condition is necessary. Maintaining the isothermal operation of the reactor drops one differential equation (energy equation) from consideration in the analysis of the obtained experimental results. The first step to achieve this isothermal condition, a rapid heat up of the gaseous reactants to the desired set point temperature. Calculations for temperature profiles of fluids under laminar flow in a straight tube have been dealt with by Kays and Crawford [106]. The solution of these calculations gives a useful insight regarding the expected gas temperature along the length of the reactor. For a situation such as the experimental facility used in this study where the reactor being placed in a temperature-controlled electric furnace representing thermal reservoir, the assumption of constant wall temperature is reasonable and at least represent the worst case scenario which corresponds to longer path for heating up the gaseous reactants. The equation for laminar flow provides the axial distribution of mass-averaged temperature (mixing cup

temperature) along the length of the reactor as a function of non-dimensional length normalized by the diameter of the tube. The solution was obtained with consideration of thermal entrance effects. However, it was assumed that the velocity profile is fully developed. For typical experimental conditions where relatively long residence time is allowed for gases that corresponds to low flow velocity and in the case of the highest set point temperature of furnace of 1773K ($T_{inlet} = 300K$ and $d_{reactor} = 0.06m$) the gases will reach the set point temperature within 4K difference at distance of 0.05 m downstream of the inlet to the tube. These predictions show that gases heated up rapidly in the reactor. This temperature distribution has been validated experimentally by measuring the temperature along the reactor length while flowing nitrogen. The measured temperature values were always within this tolerance, which validate the predictions made using this equation. It also provided a tool to predict the temperature distribution inside the reactor as well as estimate the beginning of the reaction to calculate the residence time.

3.4. Calibration of Experimental Facility

Pyrolysis of H_2S and N_2 mixtures was examined using a mixture of 5% H_2S /95% N_2 injected into the reactor. The residence time in the reactor was kept constant at 1.5s while the temperature of the reactor was changed incrementally from 1273 – 1473 K. Gas composition at the exit of the reactor were quantified during all the experiments. The input and reactor operational conditions were chosen to facilitate comparison with experimental data from the literature. The chosen residence time of 1.5s also meant that comparison with equilibrium simulation was feasible. The conversion of H_2S at different temperatures resulted in different amounts of hydrogen

production. Figure 4 shows a comparison of hydrogen production from the pyrolysis of 5% H₂S/95% N₂ mixture. The results are also compared to the data reported by Binoist et al. [67]. Since the residence time was high enough for the reaction products to reach equilibrium, a comparison is also made with equilibrium simulations. The equilibrium simulations were conducted using the chemical Equilibrium code from NASA Glenn research center [107].

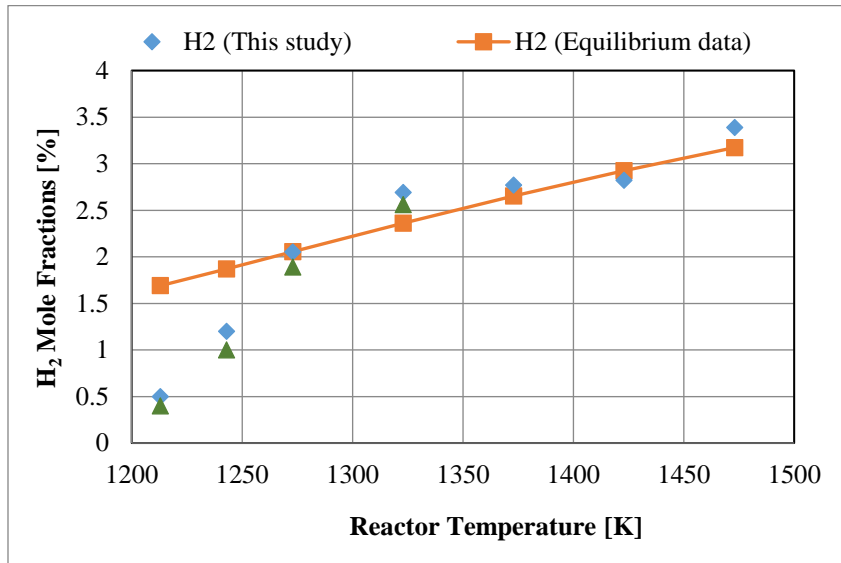


Figure 4. Comparison of experimental and equilibrium data from pyrolysis of 5% H₂S/95% Ar or N₂

Our data showed a satisfactory agreement with the data reported by Binoist et al. [67], between 1273 and 1373 K. However, they did not examine temperatures above 1373K, but our data compares well with the equilibrium predictions at these higher temperatures (above 1375 K). The equilibrium prediction matched well with the experimental data, except for temperatures below 1273 K. The production of hydrogen was undepreciated at lower temperatures, signifying that the residence time of 1.5s was not sufficient for the reactions to reach equilibrium values. Overproduction of H₂ above

equilibrium value at 1323 K and 1473 K could be due to complex chemistry that is precluded in the equilibrium calculation.

3.5. Experimental Error Analysis

Sources of errors associated with experimental measurements divides into two categories: systematic error in all measuring and controlling apparatuses, and the random error presented in our experimental measurements.

Sources of systematic error in this research were as follows:

- Thermocouple
- Gas Chromatograph (TCD and FPD)
- Flow Controllers

Table 3 shows the error in all apparatuses used in this research. It can be seen that, error ranges are very minimal so that they all lie within the experimental data points symbol represented in figures.

For random error, average time required for each experiment to be performed was 6 hours or more. Therefore, it was not possible to repeat each experiment enough number of times so that we could calculate the mean and standard deviation for each experiment. Consequently, random error assessment has been achieved via data repeatability check. All experiments performed in this research have been repeated three times or more and the average value was presented. Maximum standard deviation was observed to be less than 0.5%.

3.6.Experimental Difficulties

During the experimental runs, experimental issues used to appear that can either force us stop the experimental run and restart it all over again or impose significant

delay in the experimental run time. This problem arise from the formation of solid sulfur or formation of carbon deposits in different places in the sampling line that leads to clogging the line. Sulfur deposits as well as carbon deposits from hydrocarbon impurities introduced to the reactor were forming in the sampling probe and sampling line. Sulfur and carbon tiny particles were able to pass through the sampling line and reach the filters at the inlet of the GC. Accumulation of these particles on these filters caused clogging and prevent the sample flow from entering the GC for analysis. Subsequently, several preventive and corrective precautions were being taken in order to lessen the chances of problems caused by sulfur and carbon deposits.

Table 3. Error range associated with experimental measurements

Device	Measured quantity	Error
Thermocouple	Temperature	+2.8 K at T=1600 K
TCD	CO, H ₂ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₈	< ± 0.1 % at concentration of 100 ppm
FPD	H ₂ S, SO ₂ , COS, CS ₂	< ± 0.1 % at concentration of 1 ppm
Flow controllers	CH ₄ , CO ₂ , N ₂ Flow rates	< ± 1 % of full scale
Flow controllers	H ₂ S, NH ₃ Flow rates	$\pm(0.8\%$ of the reading + 0.2% of full scale)

Chapter 4: Results and Discussions

Experimental investigations discussed in this chapter are divided into two major sections. The first section is dedicated to hydrogen production from pyrolysis and partial oxidation of hydrogen sulfide alone. The second section represents production of hydrogen via pyrolysis of contaminated hydrogen sulfide with one impurity of the impurities naturally existing in hydrogen sulfide stream separated from natural gas such as: carbon dioxide, methane, benzene, and xylene.

4.1. Production of Hydrogen from Hydrogen Sulfide Pyrolysis and Partial Oxidation

Investigation of hydrogen production from a stream of hydrogen sulfide only has been conducted under different temperatures and inlet compositions. This will help us to understand more information on effect of each parameter. Studying the pyrolysis of hydrogen sulfide alone will also help the understanding the effect of presence of different contaminants. On the other hand, pyrolysis of hydrogen sulfide has high energy demand. An exploration of the potential of production of hydrogen via partial oxidation of hydrogen sulfide is also provided.

4.1.1. Hydrogen Production via Pyrolysis of Hydrogen Sulfide

Investigation on thermal decomposition of hydrogen sulfide has been conducted in near isothermal reactor. The effect of different reactor operational parameters including reactor temperature and inlet partial pressure has been examined. The results on the effect of reactor operational parameters on the pyrolysis of H_2S diluted with nitrogen gas were examined and are presented here. The specific

parameters examined were temperature, residence time and inlet hydrogen sulfide concentration. Role of temperature and residence times are presented first, and subsequently, results on the effect of H_2S inlet concentration in the $\text{H}_2\text{S}/\text{N}_2$ mixture on pyrolysis process are presented. The objective was to examine the pyrolysis of high concentrations of H_2S and the effect of reactor temperature on the conversion process.

4.1.1.1. Effect of Reactor Temperature and Residence time

Pyrolysis of H_2S and N_2 mixtures was examined using a mixture of 5% $\text{H}_2\text{S}/95\% \text{N}_2$ injected into the reactor. The effect of residence time and temperature of the reactor was examined. Figures 5-6 show the conversion of H_2S and amounts of H_2 produced at different residence times of the gas in the reactor at three different temperatures of 1273, 1373 and 1473K.

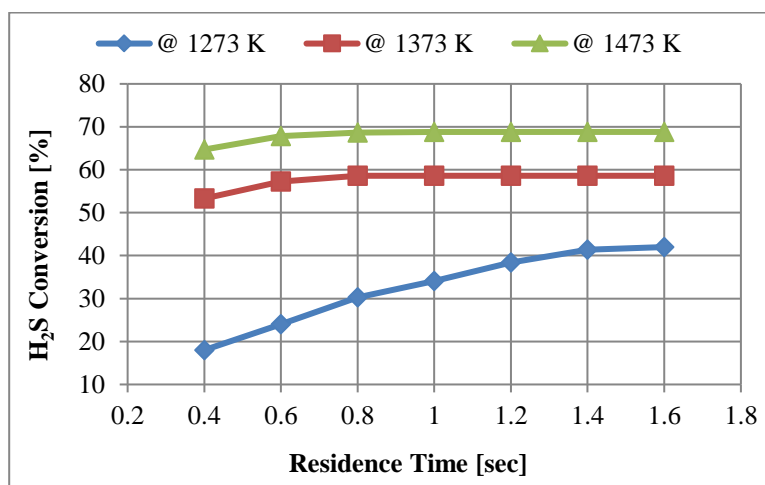


Figure 5. H_2S conversion from pyrolysis of 5% $\text{H}_2\text{S}/95\% \text{N}_2$ at different residence times in the reactor at 1273, 1373 and 1473K.

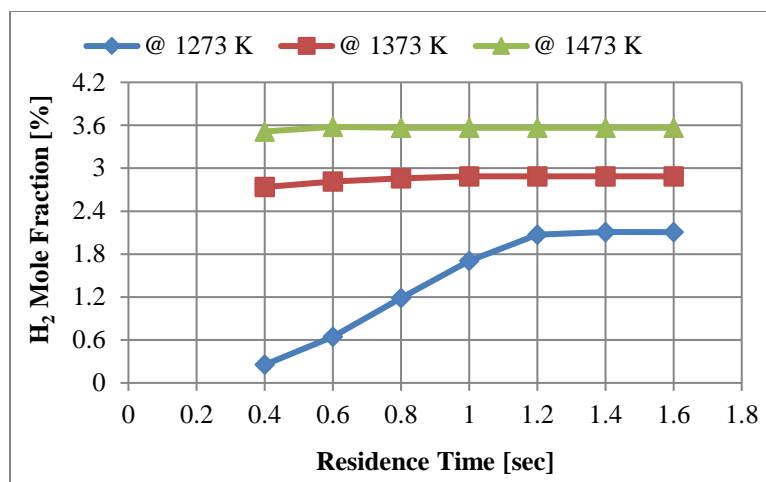


Figure 6. H₂ production from pyrolysis of 5% H₂S/95% N₂ at different residence times in the reactor at 1273, 1373 and 1473K.

The results show that the time required to reach the equilibrium state of H₂S and H₂ produced is much shorter at higher temperatures. At reactor temperatures of 1373 K and 1473 K, a residence time of 0.8s is required to reach the asymptotic state, while much higher residence time of up to 1.4s was required at 1273 K. The conversion of H₂S at higher reactor temperatures examined was between 58-69%, while at lower temperature of the reactor only up to 40% H₂S conversion was achieved.

Subsequently, a broader temperature range of the reactor (1273 – 1473 K) was examined and at a constant residence time of 2s in the reactor. Figure 7 shows the gas speciation at the exit of reactor at different temperatures and constant residence time of 2s. The results show that a residence time of 2s was enough for conversion to reach the asymptotic equilibrium values. Therefore, a comparison with equilibrium simulations data was feasible that also served to quantify the performance of the experimental facility, see Figure 7. Our results showed good agreement with the equilibrium data as well as the experimental results reported in the literature. The amounts of H₂S

conversion within the examined temperature range of 1273-1473 K were between 43-68% (Figure 5). The rate of H_2S conversion significantly increased at higher temperatures (above 1423 K) as observed from the dramatic change in slope of the graph shown in Figure 7.

The equilibrium prediction matched well with the experimental data, except for temperatures below 1273 K. The slight overproduction of H_2 above equilibrium value at 1323 K and 1473 K could be due to complex chemistry that is precluded in the equilibrium calculation. The deviation between equilibrium and experimental data at reactor temperatures below 1273 K is attributed to slow rate of chemical reactions that signifies that residence time of 2s is grossly inadequate for reactions to reach equilibrium state.

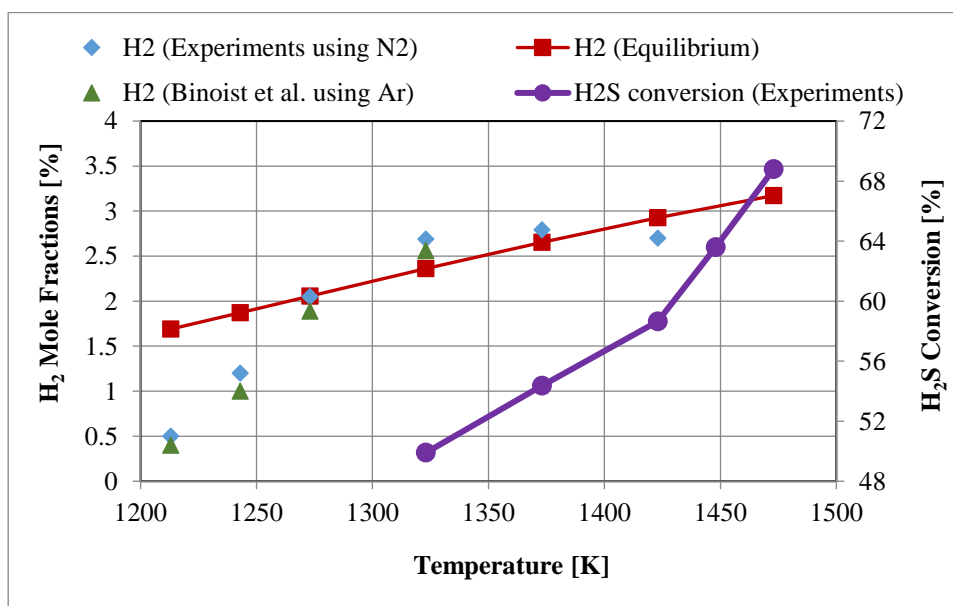


Figure 7. Comparison of experimental and equilibrium data from pyrolysis of 5% H_2S /95% Ar or N_2 .

The results reveal that pyrolysis of H_2S to produce H_2 and S_2 should be conducted at higher temperatures, wherein short residence time in the reactor favors

high conversion of H_2S . This will enable the design of more compact reactor units for the treatment of acid gas to produce hydrogen and also recover sulfur.

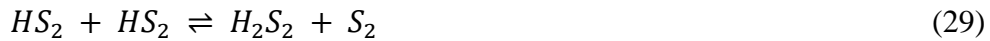
4.1.1.2. Effect of Inlet H_2S Concentration

The effect of inlet composition of H_2S on the production of H_2 was also characterized and compared with the equilibrium data. Experiments were conducted at different temperatures and constant residence time of 1.2s in the reactor. The quantity of H_2 produced was quantified and compared with the equilibrium data. Figures 8-11 show the H_2 produced with change in the inlet concentrations of H_2S in the $\text{H}_2\text{S}/\text{N}_2$ mixtures at different temperatures (1273-1573 K).

The results showed an increase in H_2 production with an increase in the amounts of H_2S in the inlet acid gas mixture. The low temperature pyrolysis data at 1273K matched well with equilibrium data. However, the deviation between the experimental and equilibrium data increased with increase in the reactor temperature and inlet H_2S concentration. This corresponded simultaneously to a decrease in H_2S conversion as the inlet concentration of H_2S was increased, see Figure 12. The results reveal the occurrence of a more complex chemistry at higher temperatures of the reactor and higher inlet H_2S concentration.

The thermal pyrolysis of hydrogen sulfide occurs via collision with another molecule M or some other radicals in the reaction pool as illustrated in reactions 22 and 23. Reaction (23) has been proven experimentally [61, 62] to be energetically favored and more dominant. Both reactions are endothermic and are favored at higher reactor temperatures. This justifies the observed increase in the H_2 production over the range of temperatures examined as well as hydrogen and sulfur radicals. Chemical

decomposition of hydrogen sulfide via reactions 24 and 25 occurs after the establishment of the radical pool in the initiation steps. This supports the observed increase in the H₂S conversion and H₂ production over the range of temperatures examined. The SH radical plays an important role in the formation of H₂ via reaction (26) which also can decompose to supply H and S radicals into the reaction pool.



However, increase in the inlet concentration of hydrogen sulfide, results in an increase in the concentration of produced radicals (such as HS, H, S, HS₂, H₂S₂) in the reactor. These radicals can then undergo recombination reactions to produce hydrogen sulfide. The significant reactions involved are summarized in the following reactions 4 and 30 through 33 to support a better understanding of the experimental data.



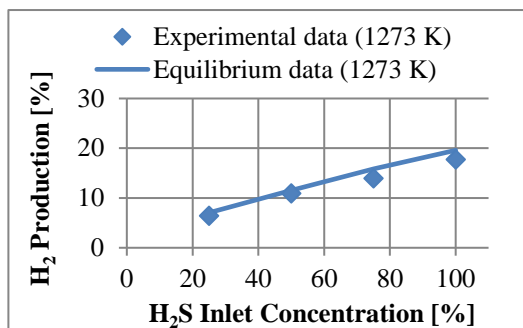


Figure 8. H₂ production with change in acid gas composition (H₂S diluted in N₂) at 1273 K reactor temperature

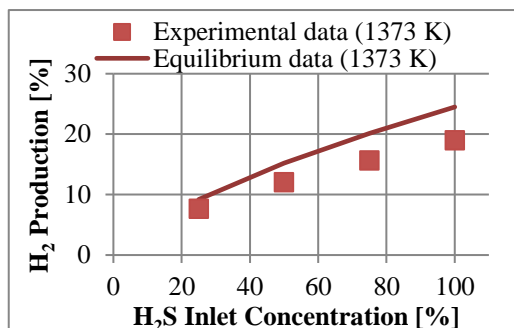


Figure 9. H₂ production with change in acid gas composition (H₂S diluted in N₂) at 1373K

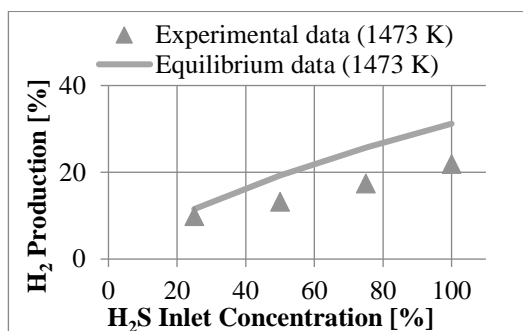


Figure 10. H₂ production with change in acid gas composition (H₂S diluted in N₂) at 1473K reactor temperature

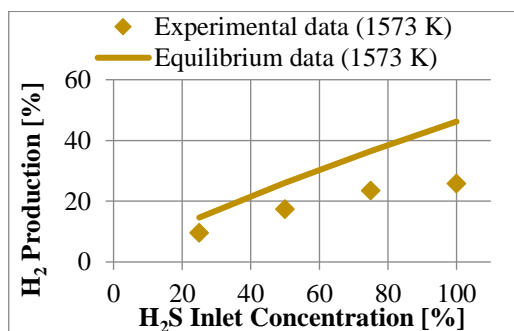


Figure 11. H₂ production with change in acid gas composition (H₂S diluted in N₂) at 1573K reactor temperature.

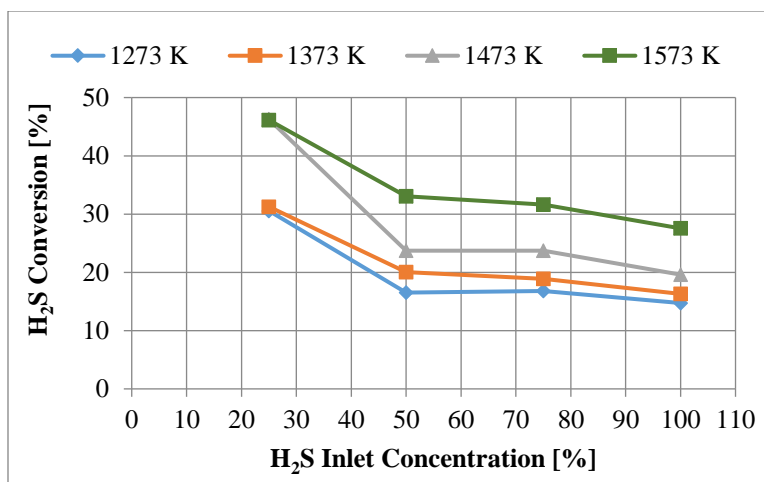


Figure 12. H₂S conversion with change in acid gas composition (H₂S diluted in N₂) and reactor temperature

Hydrogen is also favored to recombine with sulfur, which results in hydrogen sulfide production. Therefore, the decrease in hydrogen production and conversion of hydrogen sulfide is attributed to the dominant role of recombination reactions involving the vast amounts of radical pool species in the reactor. Moreover, the role of these radicals will also increase with increase in the reactor temperature, and these conjectures are evident from the greater discrepancies between experimental and equilibrium data that was observed at higher temperatures (see figures 8-11).

4.1.2. Simulation and Validation of Hydrogen Production from Hydrogen Sulfide Pyrolysis

The explanation provided in the previous section was based on the understanding of the literature. Then, we decided to simulate the obtained results numerically to determine what are the most reactive species and the most dominant reaction. Therefore, in this section, a kinetic model on hydrogen sulfide pyrolysis has been developed. This kinetic model was validated against experimental data shown in

section 4.1.1. The good matching achieved between simulation results and experimental data under the examined conditions facilitated identification of the most dominant pathways in the reaction.

4.1.2.1. Kinetics simulation

Binoist et al. [67] developed a detailed mechanism for the H₂S pyrolysis diluted in argon (95%) in a continuous perfectly mixed reactor over a residence time of 0.4-1.6s and temperatures of 1073-1323K. The detailed reaction mechanism was used to carry out numerical simulations and the results were compared with the experimental data, using CHEMKIN software package. First, numerical simulations were conducted based on Binoist [67] mechanism. However, there was poor agreement between the simulations and the experimental data at 1373 K and also at higher temperatures. Kinetics parameters in Binoist's mechanism were modified with values from Nguyen and co-workers [108] and Gargurevich [109]. Some minor changes to the pre-exponential factor were made to fit the experimental results. The modified detailed mechanism is presented in Table 4. In this investigation, plug flow reactor (PFR) model was used in the numerical simulation. It is assumed that pressure is constant in the PFR and equal to the atmospheric pressure and there are no heat losses. Experiments were performed with 5% H₂S diluted with 95% N₂. Numerical simulations were conducted under the conditions and mixture composition similar to those of the experiments.

4.1.2.2. Results and Discussion

The results on the effect of reactor temperature on the pyrolysis of hydrogen sulfide diluted with nitrogen gas were simulated numerically and validated with the

experimental data. These results confirm the validity of the modified mechanism over the investigated operating conditions at temperatures up to 1473 K.

Table 4. Detailed mechanism of H₂S pyrolysis with the rate equation: $k=A.T^b.\exp(-$

$$E_a/(RT)) [\text{cm}^3.\text{s}^{-1}.\text{mol}^{-1}].$$

Reactions	A (cm ³ .s ⁻¹ .mol ⁻¹)	b	E _a (cal.mol ⁻¹)	Ref.
H ₂ S + M = H + SH + M	1.76E+15	0.00	66200	[67]
H ₂ S + M = H ₂ + S + M	2.24E+22	-2.61	88995	[108]
N ₂ /1.5/SO ₂ /10/H ₂ O/10	(Enhanced collision efficiency)			
H + SH = H ₂ + S	1.29E+13	0.00	7210	[67]
reverse	2.00E+14	0.00	76600	[109]
H + H ₂ S = H ₂ + SH	2.90E+14	0.00	13000	[67]
reverse	1.42E+13	0.00	16340	[108]
H ₂ S + S + M = H ₂ S ₂ + M	3.60E+12	0.00	0	[67]
reverse	3.00E+20	-1.00	52800	[67]
SH + H ₂ S ₂ = H ₂ S + HS ₂	5.20E+14	0.00	6100	[67]
reverse	6.80E+14	0.00	29700	[67]
SH + HS ₂ = H ₂ S + S ₂	6.27E+03	3.05	-1105	[108]
reverse	4.80E+13	0.00	38400	[67]
SH + S + M = HS ₂ + M	6.00E+11	0.00	0	[67]
reverse	6.00E+12	0.00	70900	[67]
H + S ₂ + M = HS ₂ + M	1.00E+18	0.00	1510	[67]
reverse	1.35E+15	0.00	31100	[108]
SH + S = H + S ₂	8.97E+15	0.00	15000	[67]
reverse	6.98E+16	0.00	31300	[67]
SH + SH + M = H ₂ S ₂ + M	3.20E+13	0.00	0	[67]
reverse	2.70E+22	-1.00	58600	[67]
SH + S ₂ = S + HS ₂	1.40E+12	0.00	33700	[67]
H ₂ S ₂ + M = H + HS ₂ + M	9.10E+19	-1.00	70200	[67]
H ₂ S + S = H + HS ₂	1.00E+15	0.00	25800	[67]
SH + SH = H ₂ S + S	7.50E+07	1.14	100	[67]
reverse	1.00E+08	1.30	17100	[67]
S+S+M=S ₂ +M	1.00E+15	0.00	0	[67]
HS ₂ + HS ₂ = H ₂ S ₂ + S ₂	6.00E+12	0.00	9100	[67]
H ₂ S ₂ + H = H ₂ S + SH	6.00E+12	0.00	5200	[67]
H + HS ₂ = H ₂ S + S	6.00E+13	0.00	8400	[67]
H + HS ₂ = H ₂ + S ₂	4.30E+13	0.00	1400	[67]
reverse	4.72E+13	0.00	57610	[67]
SH + M = S + H + M	6.00E+12	0.00	73600	[67]
reverse	3.60E+15	0.00	9300	[67]
S + H ₂ S ₂ = SH + HS ₂	6.00E+12	0.00	8200	[67]

The results show that high temperatures are more favorable for hydrogen sulfide pyrolysis, similar to that reported by Hawboldt et al. [46] and Palma et al. [110]. Moreover, the modified reaction mechanism fits better with the experimental results at temperature as high as 1473 K. Hydrogen yield also increased with the increase in temperature along with decreased residence time to reach the asymptotic steady state value.

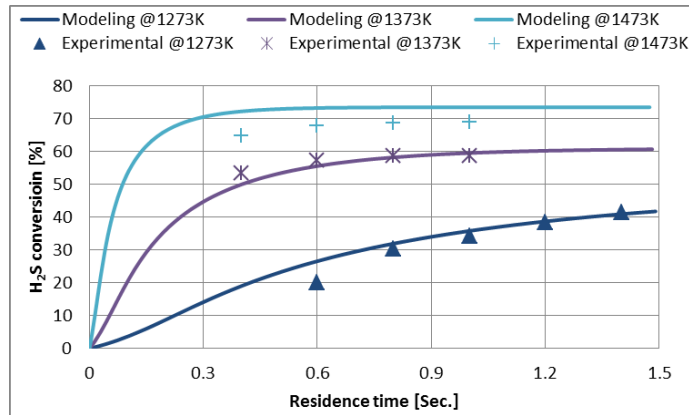


Figure 13. Comparison between modeling and experimental data on H₂S conversion

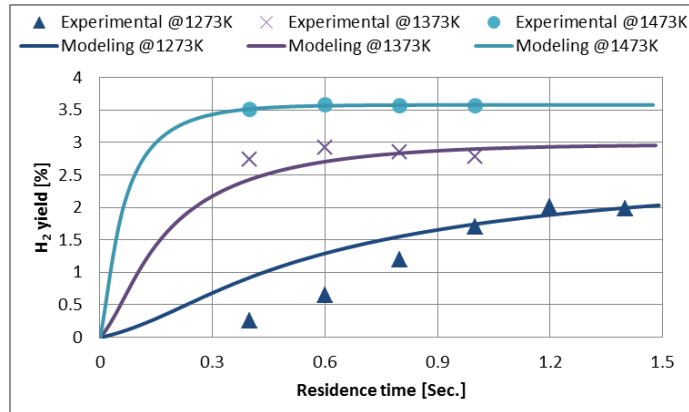


Figure 14. Comparison between modeling and experimental data on H₂ yield

Based on the qualitative agreement between the experimental data and the numerical simulations using the modified reaction mechanism over the investigated operational conditions, reactions pathways and the most dominant reactions in the

decomposition of hydrogen sulfide and formation of products can be determined. From the analysis of the reactions pathways, we find that at low mean residence time the dissociation is initiated via collision of molecules according to the following reactions:



Once the pool of radicals is established, reaction (24) takes place when consumption of hydrogen sulfide and production of hydrogen occurs via the collision between hydrogen sulfide and hydrogen radical. Propagation of the reaction is carried out through the radicals produced in reactions (22-24).



A close examination of the chemical reaction pathways allowed us to deduce that reaction (24) is the dominant in the conversion of hydrogen sulfide to hydrogen during the reaction. Hydrogen radical plays a significant role in the decomposition process, this radical attacks hydrogen sulfide to produce hydrogen and SH radical. SH radical is amongst the radicals responsible for sulfur formation through the following reactions:

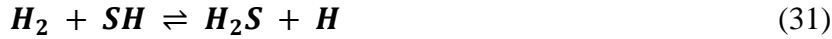


Hydrogen radical also participates in breaking down other radicals as shown in reaction (36). HS₂ radical also plays an important role that also participates in the formation of sulfur as well as the other radicals via the following reactions:





Once the pool of radicals has been established and the reaction became more reactive, the recombination reactions between the products become more significant (via the reverse of the initiation reaction direction with the increase of residence time, as follows):



4.1.2.3. Summary

Experimental results on the production of hydrogen from pyrolysis of diluted and non-diluted hydrogen sulfide stream were presented. The optimum operating conditions that favor hydrogen production and high conversion of hydrogen sulfide were investigated. The results show significant role of reactor residence time and reactor temperature, as well as inlet concentration of hydrogen sulfide injected into the reactor. A high reactor temperature significantly reduces the reactor residence time required for high conversion of hydrogen sulfide. At temperatures above 1373 K, conversion of hydrogen sulfide reached an asymptotic steady state value at a residence time of approximately 0.8s, while more than 1.2s residence time was required to attain such a steady state asymptotic value at 1273 K. Increase in the inlet concentration of hydrogen sulfide enhanced the radical pool species and stimulated recombination reactions that hindered hydrogen production and hydrogen sulfide conversion. This was apparent from the increased deviation between equilibrium and experimental data as the inlet concentration of hydrogen sulfide and temperature of the reactor were increased.

The obtained experimental results of pyrolysis of hydrogen sulfide has been studied numerically using a plug flow reactor model. Experimental results obtained at temperatures up to 1473 K using a plug flow tubular reactor were used to validate the model simulations. A detailed reaction mechanism has been modified to simulate the thermal dissociation of hydrogen sulfide. A comparison between experimental data and simulation results revealed the validity of the mechanism on simulating the pyrolysis of hydrogen sulfide over the investigated conditions. The qualitative agreement between the experimental results and simulations provided possible identification of the various reaction pathways as well as the most dominant reactions. The proposed reaction mechanism has been validated for simulating hydrogen sulfide dissociation.

4.1.3. Hydrogen Production from Hydrogen Sulfide Partial Oxidation

The potential of hydrogen production from hydrogen sulfide oxidation in temperature range of 1273-1473K and at high equivalence ratio has been investigated. This method has less energy requirement than pyrolysis since thermal energy required for the pyrolysis is partly supplied by the oxidation of a portion of the hydrogen sulfide.

4.1.3.1. Effect of Presence of Oxygen on Hydrogen Sulfide Pyrolysis

Experimental results on effect of oxygen injection on pyrolysis of hydrogen sulfide stream diluted with nitrogen at reactor temperatures in the range of 1273-1473 K at different residence times are examined. The composition of the inlet stream is 9% H_2S / 1% O_2 / 90% N_2 . However, the oxidation reaction was very rapid to be captured and concentration did not change much with the residence time so that results on only composition at residence time of 1.2 sec are reported, see Figure 15. A comparison between pyrolysis of a stream of hydrogen sulfide with oxygen and without oxygen on the amounts of H_2 produced is shown in Figure 15 while Figure 16 shows the H_2S

conversion. Results shown in Figure 15 confirm that production of hydrogen from pyrolysis of hydrogen sulfide stream is favored at higher temperatures in both cases of hydrogen sulfide alone and hydrogen sulfide with traces of oxygen. The hydrogen produced decreased by some 37% with oxygen injection as compared to that without oxygen.

Reaction with oxygen has three routes, one of them being oxidation of hydrogen sulfide to produce sulfur oxides and water vapor. The other routes being reaction with one of the products hydrogen (to produce water vapor) or sulfur (to form sulfur oxides). Initially, oxidation reaction occurs between oxygen and hydrogen sulfide till hydrogen and sulfur molecules or radicals form then a competition between the products and hydrogen sulfide occurs. Based on the comparison between the reaction rates of oxidation of hydrogen sulfide and hydrogen, oxygen favors reaction with hydrogen sulfide. Thus, the main reason behind the decrease in hydrogen produced is not due to the direct oxidation of hydrogen produced. The direct oxidation occurs in hydrogen sulfide to form water vapor and sulfur oxide while the remaining hydrogen sulfide decomposes to hydrogen and sulfur. Reduction reaction between hydrogen produced and sulfur oxide consumes hydrogen produced to reduce the amounts of hydrogen produced. This is similar to reactions occurring at the catalytic stages of Claus reactor. This conjecture is also supported by the absence of any sulfur oxide peaks from the gas analysis.

The amounts of hydrogen produced decreased while the conversion of hydrogen sulfide increased. This is due to the fact that the presence of oxygen consumes one of the products of the pyrolysis which thermodynamically shifts the equilibrium

towards more consumption of hydrogen sulfide. This explains the increased conversion of hydrogen sulfide in the presence of oxygen more than the absence of oxygen, as shown in Figure 16.

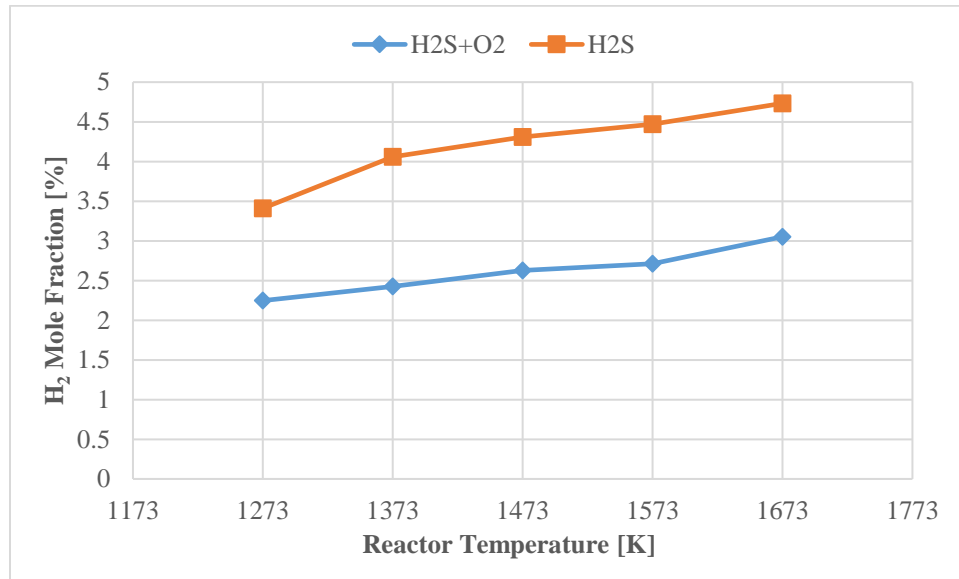


Figure 15. A comparison on the amounts of hydrogen produced from H₂S only and H₂S with O₂

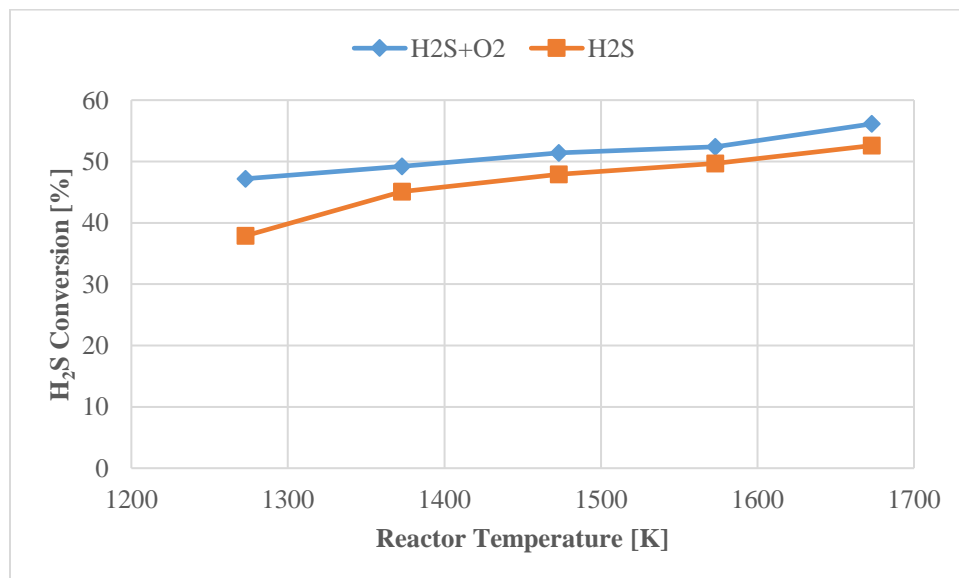


Figure 16. Comparison of H₂S conversion of H₂S only and H₂S with O₂

4.1.3.2. Effect of Oxygen Composition on Hydrogen Sulfide Pyrolysis

The effect of different amounts of oxygen on hydrogen sulfide pyrolysis has also been investigated. The pyrolysis of two streams with 1% oxygen (mixture of 9% H₂S/1% O₂) and the 2% oxygen (8% H₂S/2% O₂) were evaluated. Also, a comparison on the pyrolysis of two streams with the same composition of hydrogen sulfide but without oxygen has also been made. Figure 17 and Figure 18 show that increase in the amounts of oxygen injected with hydrogen sulfide decreases the amounts of hydrogen produced. This is attributed to the oxidation of more hydrogen sulfide to sulfur oxide that consumes the produced hydrogen to result in reduced hydrogen production. This also means that increase in the amounts of oxygen introduced to the reaction increased the conversion of hydrogen sulfide as shown in Figure 18.

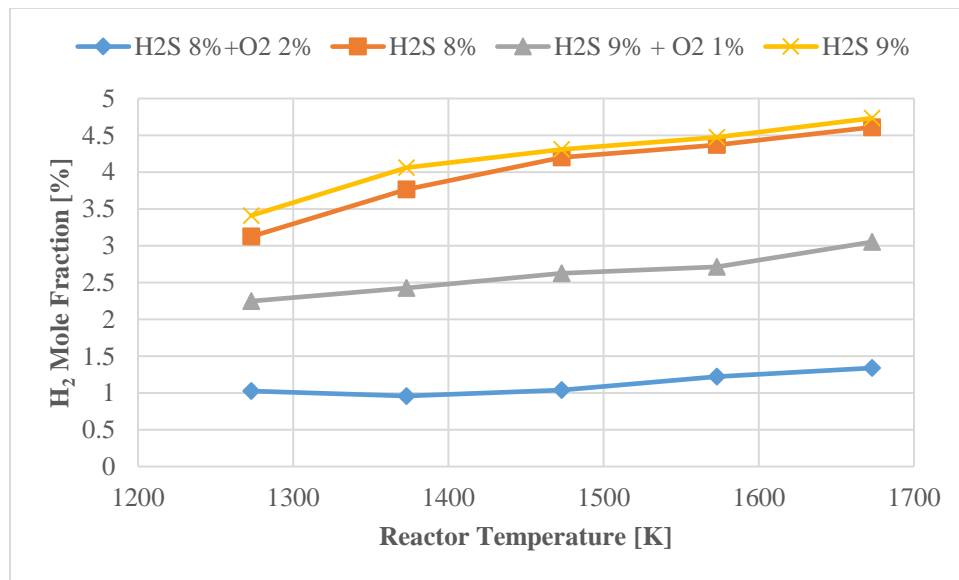


Figure 17. A comparison on the amounts of hydrogen produced from H₂S only and H₂S with O₂

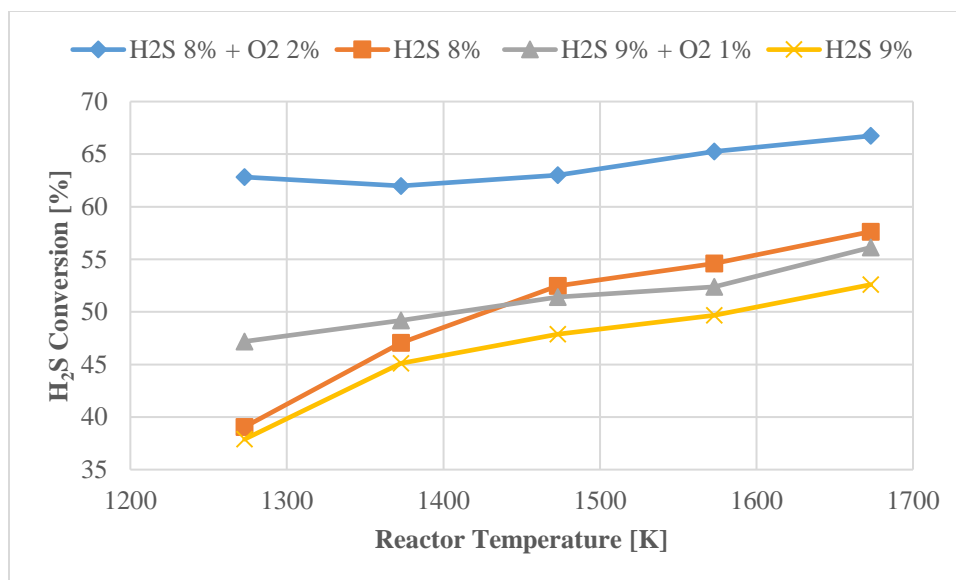


Figure 18. Comparison of H₂S conversion of H₂S only and H₂S with O₂

4.1.3.3. Summary

Potential of hydrogen production via partial oxidation of hydrogen sulfide has been shown experimentally in a tubular reactor over temperature range of 1273-1473 K. A comparison between amounts of hydrogen produced both without and with oxygen injection has been made along with hydrogen sulfide conversion in each case. Results showed higher conversion of hydrogen sulfide with injection of oxygen. Production of hydrogen was lower in presence of oxygen due to partial consumption of hydrogen formed to H₂O. The absence of SO₂ with oxygen present in the hydrogen sulfide stream was featured at all the temperature investigated. These results provide a window of favorable operational conditions for hydrogen production via partial oxidation of hydrogen sulfide. These results also provide viable development of this treatment method as a standalone method or as part of hybrid operation in conjunction with the Claus reactor.

4.2. Pyrolysis of Contaminated Hydrogen Sulfide

Based on the understanding of the pyrolysis of hydrogen sulfide in the previous sections, effects of presence of different contaminants on the reformation of hydrogen sulfide to produce hydrogen will be investigated in the later sections. Since carbon dioxide is the major contaminant in hydrogen sulfide, pyrolysis of acid gas to produce syngas is investigated. Other hydrogen-constituted impurities naturally present in hydrogen sulfide stream separated from crude oil and gas wells such as methane, benzene, xylene were mixed with hydrogen sulfide to evaluate the role played by their presence in the mixture on amounts of hydrogen produced and conversion of hydrogen sulfide.

4.2.1. Syngas Recovery from Acid Gas Stream Composed of H₂S and CO₂

The results on the pyrolysis of H₂S and CO₂ diluted in nitrogen were examined and are presented. The goal here was to quantify experimentally the speciation of syngas (H₂ and CO) production from the pyrolysis of acid gas (H₂S and CO₂) over a range of temperatures and gas composition.

4.2.1.1. Effect of Reactor Temperature on Pyrolysis of Acid Gas

Pyrolysis of acid gas mixture was examined in the plug flow reactor over a temperature range of 1323 K to 1473 K at high residence times of 2s. The objective was to examine the effect of temperature on the syngas (H₂ and CO) composition. However, investigating higher reactor temperature and its effect on CO₂ derivate species was not the scope in this study. The result of produced syngas composition at different temperatures is shown in Figure 19. These results are shown with 3% H₂S/2%

CO₂/95% N₂, which represents 60% H₂S and 40% CO₂ in the H₂S/CO₂ acid gas mixture since the N₂ is inert. The ratio of H₂ to CO is observed to reduce while the syngas production increases with increase in reactor temperature. Production of CO was very minimal at temperatures below 1373 K. A reactor temperature less than 1373 K favors syngas yields with high H₂ content. If the requirement is to utilize only the produced H₂, through the use of suitable separation techniques, then lower reactor temperatures (below 1450 K but not lower than 1200 K) are considered to be preferable. However, it is important to also note that lower reactor temperatures result in higher amounts of H₂S emission from low conversion of both H₂S and CO₂, even when sufficient residence time is available. Note that different composition of syngas is required for different applications since high ratio of H₂ to CO is not suitable for certain applications while in other applications they are favorable.

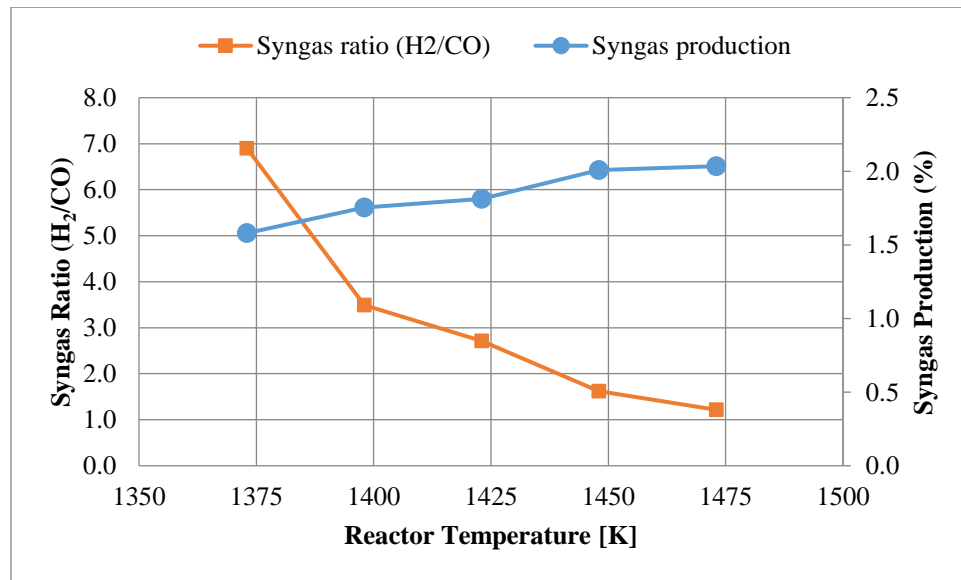


Figure 19. Effect of reactor temperature on Syngas production (3% H₂S/2% CO₂ diluted in 95% N₂)

Syngas gas produced can be used for gas engine application and liquid fuels production. For example, Table 5 shows the specifications of syngas for Siemens gas plants application [111]. Siemens energy gas plants require syngas with a ratio of H_2 to CO between 0.5 and 1.1 for successful operation and similar ratio is required for production of ammonia. The effect of inlet composition of acid gas (H_2S/CO_2 ratio) on the composition of syngas (H_2 and CO) was also examined at a reactor temperature of 1473 K and residence time of 2s.

Table 5. Specification of syngas for Siemens gas plants [111]

Fuel gas component	Gas turbine V94.2	Gas turbine V94.3	Gas turbine 2xV94.2K
H_2	12.3	10.7	31.3
CO	24.8	29.2	28.5
CO_2	0.8	1.9	3.2
N_2	42.0	53.1	-
H_2/CO	0.5	0.36	1.1
LHV(MJ/Kg)	4.3	4.3	9.1

Figure 20 shows the composition of syngas evolved with change in the inlet composition of acid gas (H_2S and CO_2), diluted in N_2 gas at reactor temperature of 1473 K and residence time of 2s. It also shows the amount of syngas produced with the variation of the inlet composition acid gas. The result showed that only a specific

composition of acid gas can produce syngas composition applicable for gas engines and for ammonia production. From Figure 20, one can see that the ratio of H_2 to CO production is dependent on the initial acid gas composition (H_2S and CO_2). This ratio decreases with increase in the amounts of CO_2 in the inlet acid gas. This demonstrates that lean acid gas (with high CO_2 content) is preferable and well suited for syngas production with a H_2 to CO ratio of 0.3 to 1.2 that meets the requirement for gas engine and ammonia production. This can help ease the operational difficulties that lean acid gases pose in the operation of Claus process. It should be taken to consideration that syngas production is decreasing with the increase of CO_2 in the inlet stream of acid gas due to the high stability of CO_2 .

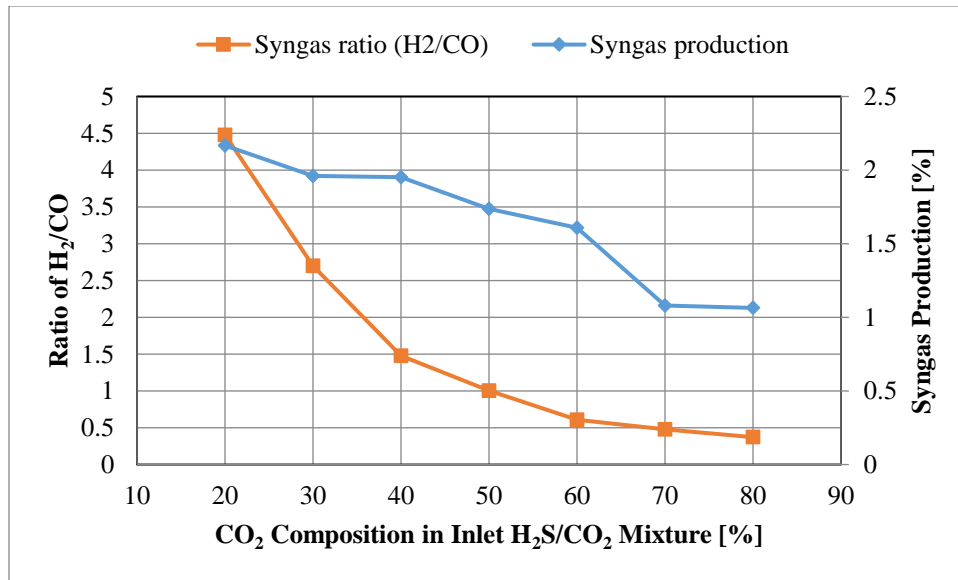


Figure 20. Effect of acid gas composition on Syngas production at 1475 K. (H_2S/CO_2 diluted in 95% N_2)

4.2.1.2. Effect of CO_2 on H_2S Pyrolysis

A direct comparison of H_2 production from the pyrolysis of diluted H_2S with mixtures of H_2S and CO_2 was conducted to isolate the effect of CO_2 in the conversion

process. The test condition for the H_2S and $\text{H}_2\text{S}/\text{CO}_2$ mixtures were examined at constant residence times of 2s and constant total volumetric flow of all injected gases (H_2S , CO_2 and N_2). Figure 21 and Figure 22 show the conversion of H_2S and production of H_2 at different reactor temperatures for the two acid gas mixtures. Pyrolysis of H_2S favored an increase in H_2 production at higher reactor temperatures (Figure 22). This also corresponded to an increase in the conversion of H_2S as shown in Figure 21. Our observed trends on H_2S pyrolysis agree favorably with the data reported in the literature [67].

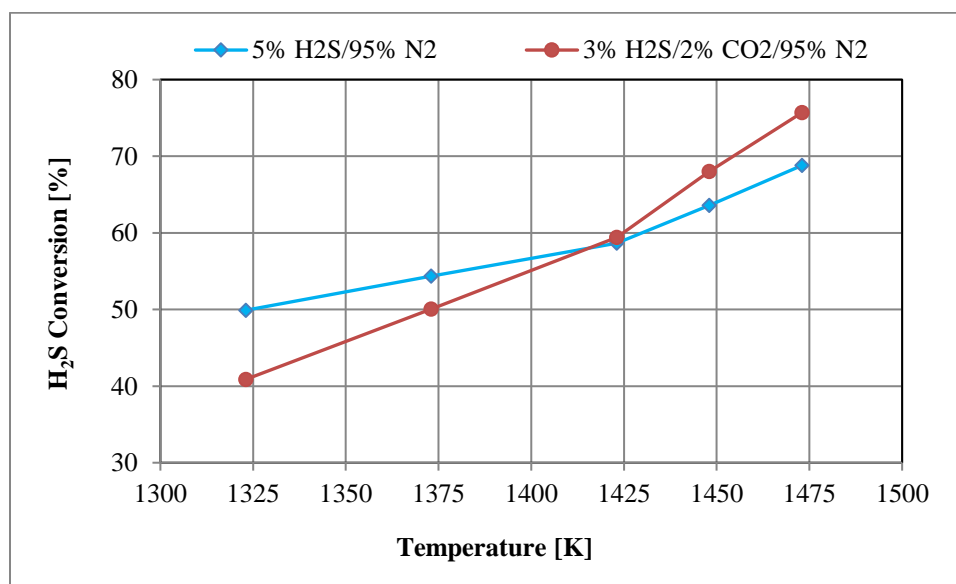


Figure 21. H_2S conversion with change in acid gas composition and reactor temperatures (H_2S or $\text{H}_2\text{S}/\text{CO}_2$ diluted in 95% N_2)

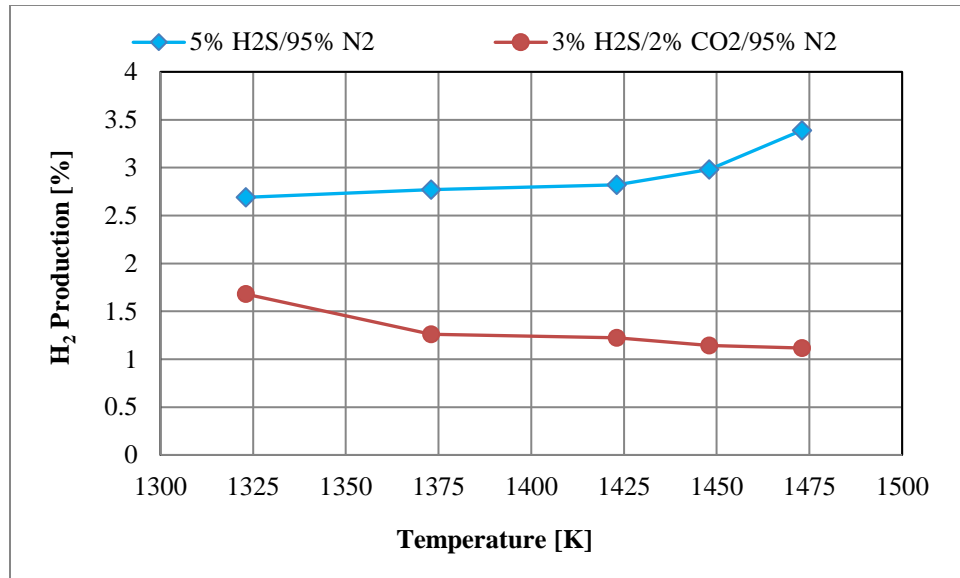


Figure 22. H₂ production with change in acid gas composition and reactor temperatures (H₂S or H₂S/CO₂ diluted in 95% N₂)

The pyrolysis of H₂S occurs via collision with another molecule M or some other radicals in the reaction pool as illustrated in reactions 22 through 29 [67, 109]. The net reactions are endothermic and are favored at higher reactor temperatures. This justifies the observed increase in the H₂ production over the range of temperatures examined. Sulfur formation was also visibly observed along the sampling lines and other cooler regions of the experimental facility.





However, there was a slow increase in the production of H_2 over a temperature range of 1323 K to 1425 K, but thereafter; faster rate of H_2 formation was observed. This could be attributed to a possible change in reaction mechanism from the faster kinetics at higher temperatures.

Addition of CO_2 into the inlet H_2S/N_2 showed decreased conversion of H_2S at temperatures below 1435 K, but the H_2S conversion increased at higher temperatures, see Figure 21. The lower conversion of H_2S at lower temperatures could be attributed to dilution effects. It is noticed that conversion of H_2S was lower within 1323 K to 1423 K, wherein only up to 20% CO_2 was converted. But as the CO_2 conversion increase up to 48%, the conversion of H_2S significantly increased. This showed that the release of oxidizer from CO_2 promoted oxidation reactions of H_2S in the reactor. Oxidation reactions were also responsible for the observed decrease in the production of H_2 with increase in temperature of the reactor. The amounts of undecomposed CO_2 at the exit of the reactor alongside CO production data is given in Figure 23. This substantiated the production of oxidizer in the reaction pool. Reactions 38 and 39 are typical significant reactions involved in the initial decomposition of CO_2 [94, 45]. Decomposition of CO_2 is an endothermic process that is favored at higher temperatures to produce CO and atomic oxygen. Another channel for CO_2 decomposition is through the radical attack by an active radical (such as H) in the reactor to produce other oxygenated radicals (see reactions 38 and 39).



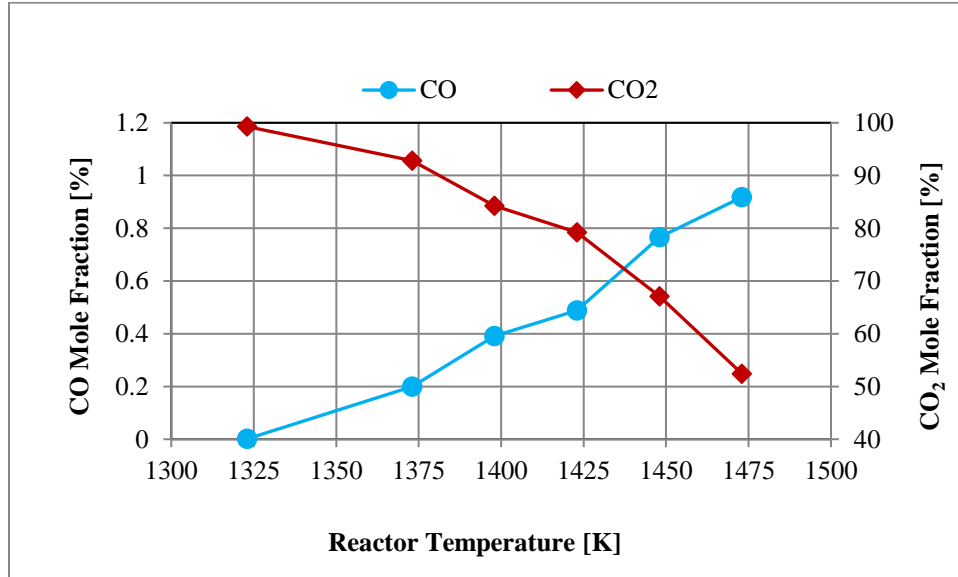
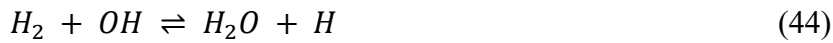


Figure 23. CO production and CO₂ fraction with change in reactor temperatures (3% H₂S/2% CO₂ diluted in 95% N₂)

The release of O and OH radicals then promotes oxidation H₂S, H₂ and other radicals formed in the reactor. Some of the possible reactions are illustrated in reactions 40 through 45 to provide better understanding of the experimental data [39]. Reactions 44 and 45 clearly shows that the observed decrease in H₂ production is due to reaction with available oxidizer (OH and O radicals) emanating from initial CO₂ decomposition in the reactor.



The importance of HS, HS₂ and H₂S₂ radicals in the pyrolysis can be clearly observed from the given plausible chemical reaction mechanism. Other radicals that include SO, OH, CS and HSO also play significant roles in the H₂S and CO₂ thermal conversion process. These radicals have to be well accounted for when developing a comprehensive mechanism for H₂S and CO₂ thermal decomposition process.

4.2.1.3. Summary

Experimental results on the syngas conversion from acid gas while also recovering sulfur are presented. The effect of reactor temperature and acid gas composition on the syngas evolved was examined over a 1250–1475 K temperature range and high residence time in the reactor. The results revealed importance of reactor temperature and acid gas composition on the conversion of H₂S and CO₂ (acid gas) to produce syngas with a wide range of H₂ to CO ratio. Presence of CO₂ in acid gas enhanced H₂S conversion and CO production while reducing H₂ production. Acid gas composition, having H₂S content lower than 60%, offers the potential for syngas production that is suitable for both gas engine application and ammonia production. The results show that pyrolysis of acid gas is well suited for the treatment of lean acid gas (having high CO₂ content), to alleviate operational difficulties with the processing of lean acid gas in Claus process. The presence of impurities, such as hydrocarbons is expected to further enhance the production of hydrogen-rich syngas. These results highlight the potential of syngas recovery for the treatment of lean acid gas. The syngas produced can subsequently be used in a wide range of applications, including gas engines, ammonia plants and liquid fuel production.

4.2.2. Reformation of Hydrogen Sulfide in Presence of Methane

Reformation hydrogen sulfide to hydrogen with methane present was examined over a temperature range of 1273 K to 1673 K in a plug flow reactor at relatively high residence times of 1.2s. Also, the effect of inlet composition has been examined at temperature of 1573 K and same residence time. The objective was to examine the effect of temperature and $\text{H}_2\text{S}/\text{CH}_4$ inlet composition ratio on production of hydrogen as well as the conversion of hydrogen sulfide to evaluate this treatment method.

4.2.2.1. Effect of Temperature on Reformation of Hydrogen Sulfide in Presence of Methane

The results on the amounts of produced hydrogen at different temperatures are shown in Figure 24. These results are with 6.667% H_2S /3.333% CH_4 /90% N_2 , which represents $\text{H}_2\text{S}/\text{CH}_4$ ratio of 2 that reflects the stoichiometric ratio in the global reaction since N_2 is inert. The production of hydrogen as well as the conversion of both hydrogen sulfide and methane were observed to increase with increase in reactor temperature. Production of hydrogen increased significantly when the temperature exceeded 1373 K due to the release of hydrogen from the complete decomposition of methane above this temperature that occurs thermally or chemically via active radicals such as H, S, SH. Methane thermal decomposition initiated with H-abstraction and methyl radical formation as expressed in reaction (46). The chemical decomposition then occurs when produced H radical attacks undecomposed methane to produce more methyl radicals as shown in reaction (47). The H radical produced plays an important role in accelerating the decomposition of both CH_4 and H_2S , as discussed here in later

section. Recombination of methyl radicals to form C₂ bonds hydrocarbon occurs and they were measured in very small quantities and hence not reported. Decomposition of these C₂ bond hydrocarbons leads to other hydrocarbon radicals and H-abstraction which supply more H radical to the reaction pool (see reactions 49-51). Also further decomposition of methyl radical with H-abstraction from it increases the H radical in the reaction pool (52-55)



Hydrogen production paths from methane are described in reactions (47,49,51,53-55,28). The production of hydrogen continued to increase with the increase of temperature even after the complete conversion of methane. However, the increase in hydrogen production with temperature after this point is at lower rate. This is attributed to enhanced H₂S consumption in the presence of methane, which will be

explained later, as well as the higher endothermicity of hydrogen sulfide decomposition.

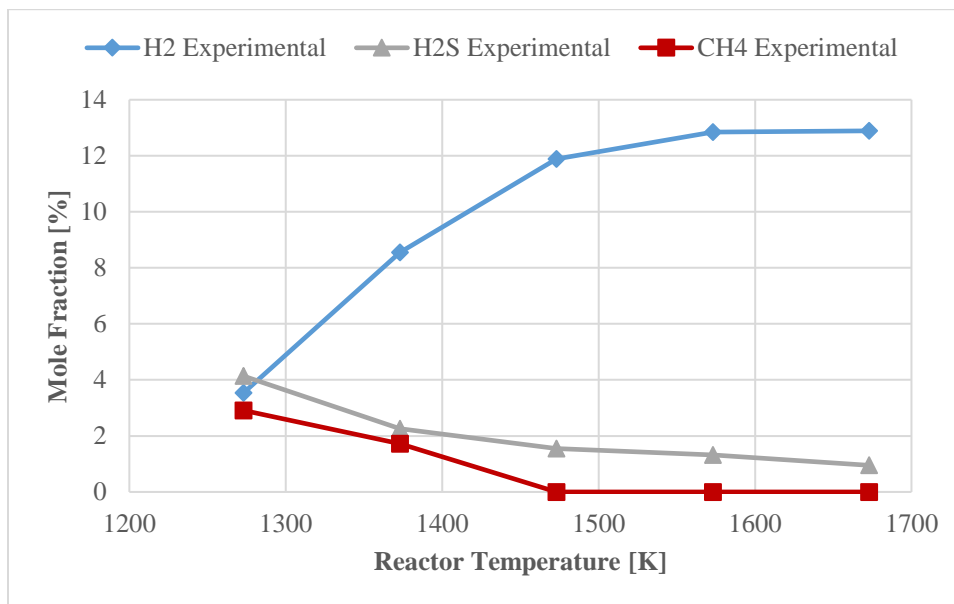


Figure 24. Effect of reactor temperature on hydrogen production

Figure 25 shows a comparison of the amounts of hydrogen produced in both decomposition cases of hydrogen sulfide only and hydrogen sulfide in presence of methane. It can be observed that at temperatures higher than 1350 K, the amount of hydrogen produced from the mixture of hydrogen sulfide and methane during reformation is much higher than that produced from thermal pyrolysis of hydrogen sulfide alone with the same amounts of hydrogen sulfide as that in the hydrogen sulfide/methane mixture. This is expected due to the higher hydrogen amounts in the feedstock of hydrogen sulfide and methane mixture than that in hydrogen sulfide alone. Also, the relatively lower stability of methane makes it easier to liberate its hydrogen at relatively lower temperature than hydrogen sulfide alone. In other words, the lower endothermicity of methane decomposition as compared to hydrogen sulfide increased the production of hydrogen from methane at lower temperature.

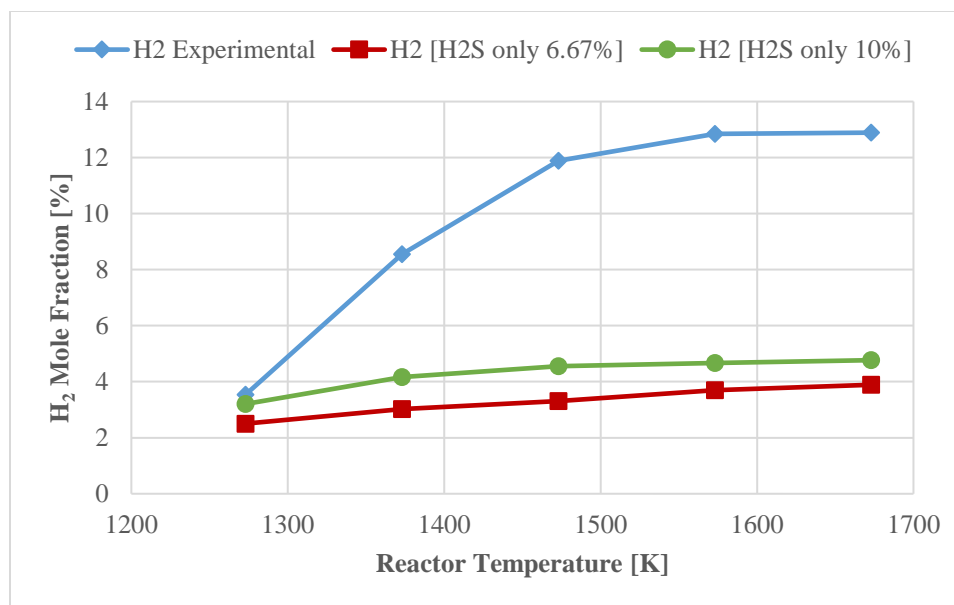


Figure 25. Hydrogen produced from hydrogen sulfide with methane and hydrogen sulfide only

However, the results in the previous figure did not answer the question whether the presence of methane affect the hydrogen sulfide pyrolysis or not. The results shown in Figure 26 on hydrogen sulfide conversion at the same inlet composition of hydrogen sulfide depicted that conversion increased in the presence of methane. The decomposition of hydrogen sulfide is known to be equilibrium limited due to occurrence of reverse reaction between produced hydrogen and recovered sulfur. However, in the presence of methane, sulfur is consumed to form other compound (CS_2), so that sulfur consumption shifts the equilibrium towards further consumption of hydrogen sulfide which makes the decomposition of hydrogen sulfide thermodynamically favored. Also kinetically, the decomposition of sole hydrogen sulfide occurs both thermally via reactions (22-23) and chemically via reaction (24, 25, 56) producing S and H radicals, more hydrogen sulfide is consumed via the following reactions:



Thermal decomposition of hydrogen sulfide increased with increase in the temperature as shown in Figure 26 for both cases of with or without methane which attempts to isolate the effect of presence of methane to increase H₂S conversion. With more hydrogen radicals in the reaction pool at relatively lower temperatures, due to the decomposition of methane at such temperatures (reactions 46-55, 28), conversion of hydrogen sulfide increased via chemical decomposition as shown in reaction (24). Karan and Behie [79] inferred that the hydrogen radical reacts faster with hydrogen sulfide than methane, which supports that reaction (24) increases the consumption of hydrogen sulfide in the presence of methane.

Generally, the interaction of hydrocarbons with sulfurous compounds leads to the incidence of plentiful lateral reactions and promotes the formation of carbonaceous-sulfurous compounds. In this case, the presence of methane with hydrogen sulfide promotes the formation of CS₂. However, the rate of CS₂ formation was limited by the hydrogen sulfide thermal decomposition which agrees with the results of Chin et al. [112] and Karan and Behie [79].

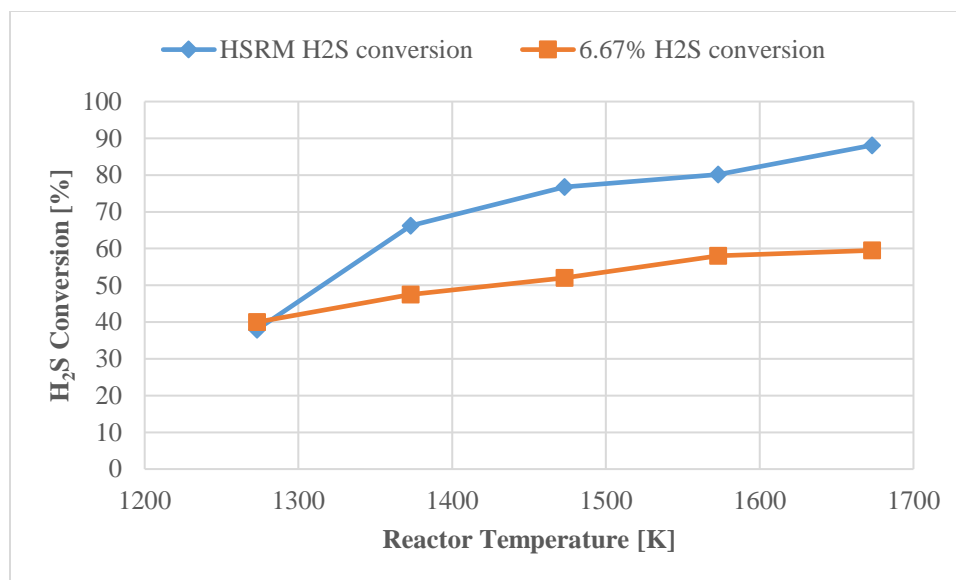


Figure 26. H₂S conversion as a function of temperature for 6.67% H₂S/3.33% CH₄ in 90% N₂ and 6.67% H₂S in 93.3% N₂ mixtures

Comparing the reaction rate constants of S and H radicals with both methane and hydrogen sulfide, it can be concluded that S and H radicals reacts more readily with hydrogen sulfide than methane. Since, the formation of CS₂ is attributed to the interaction of methane and other hydrocarbon radicals with sulfur species, then it is expected that SH to be the major sulfurous radical for CS₂ formation as shown in reaction (57). However, reactions (58-60) are also possible channels for the formation of CS₂.

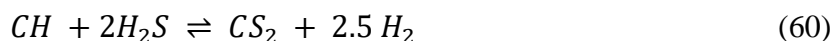


Figure 27 shows composition of carbon disulfide evolved with change in the reactor temperature from 1273 K to 1673 K and residence time of 1.2s.

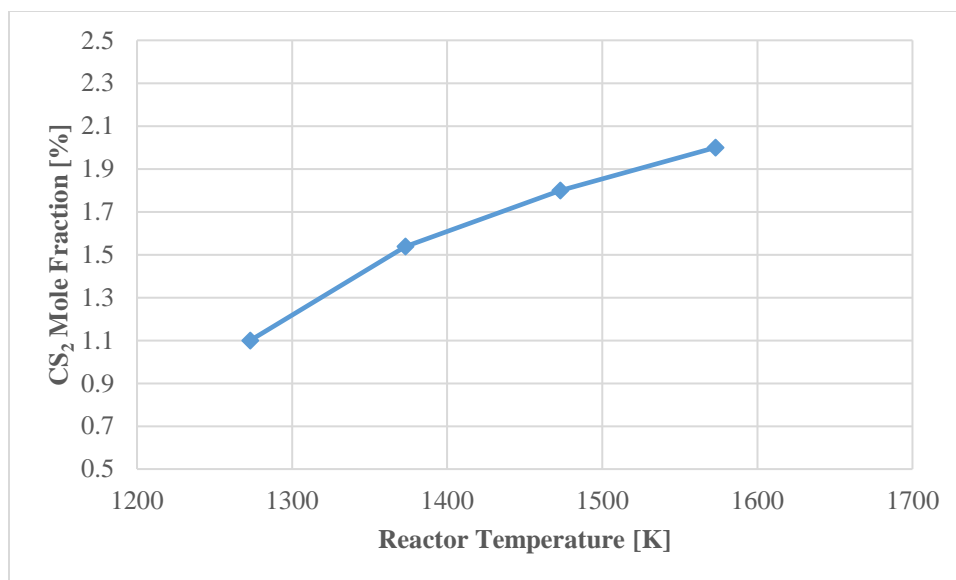


Figure 27. Effect of reactor temperature on Carbon disulfide formation

It can be observed that the formation of carbon disulfide is unavoidable in this process due to the presence of methane while sulfur is liberated from hydrogen sulfide during hydrogen formation. The formation of CS₂ byproduct increases with increased decomposition of hydrogen sulfide due to the abundance of SH radical as well as sulfur or sulfurous radicals in the reaction pool because it appears that the thermal decomposition of hydrogen sulfide is from the rate limiting step of CS₂ formation.

4.2.2.2. Effect of CH₄ Composition on H₂S Pyrolysis

Carbon deposits were visually observed on the inner surface of the reactor from 6.67% H₂S/3.33% CH₄/90% N₂ at all the temperatures investigated, see Figure 28. This carbon deposits forms due to abundance of carbon and relative scarcity of sulfur to form gaseous CS₂ byproduct rather than carbon deposition on the surface. The abundance of carbon is attributed to the complete conversion of methane at temperatures lower than those of hydrogen sulfide which is governed by the lower endothermicity of methane pyrolysis than that of hydrogen sulfide pyrolysis. In

addition, decomposition of 2 molecules of hydrogen sulfide as compared to only 1 molecule of methane is required to form carbon disulfide. The problems associated with carbon deposits pertain to the poisoning of catalysts used to accelerate this reaction. To avoid these problems, carbon deposits should be eliminated. One route to eliminate carbon deposition is to achieve conversion of hydrogen sulfide equal to twice the conversion of methane using mixture ratio of $\text{H}_2\text{S}/\text{CH}_4$ as 2. On the other hand, decreasing the methane composition in the inlet stream can limit the carbon constituent introduced to the reactor which can not only eliminate the carbon deposition but also reduce the formation of CS_2 . The effect of different amounts of CH_4 was examined in a plug flow reactor at temperature of 1573 K and at relatively high residence times of 1.2s. The objective was to examine the effect of methane amounts on the formation of CS_2 and carbon deposits. Hydrogen sulfide to methane ratio of 2 was to reflect the stoichiometric composition and also represents a base case for other compositions. Figure 29 shows the amount of hydrogen produced and the remaining undecomposed hydrogen sulfide for different $\text{H}_2\text{S}/\text{CH}_4$ ratios from a 10% $\text{H}_2\text{S}/\text{CH}_4$ mixture diluted in 90% N_2 . It can be observed that the amount of hydrogen produced decreased with increase in hydrogen sulfide amounts in the mixture. This decrease in hydrogen produced is due to the reduced hydrogen constituent in the mixture with the reduced methane amounts in the mixture. It can also be observed that the amount of hydrogen sulfide in the product stream increased with the increased amounts at the inlet stream.



Figure 28. Carbon deposition on the inner walls of the reactor

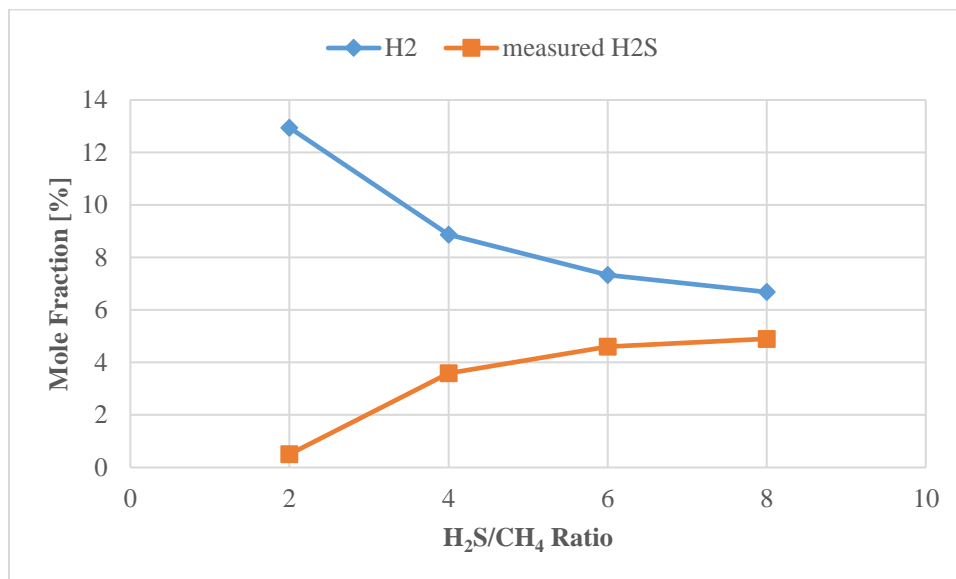


Figure 29. H₂ and H₂S with change in H₂S/CH₄ ratio (H₂S/CH₄ diluted in 90% N₂)

This decrease in the conversion of hydrogen sulfide with the increase of hydrogen sulfide amounts (or decrease of methane amounts) in the inlet stream shown in Figure 30 can be attributed to limited effect of the presence of methane on the conversion of hydrogen sulfide. Decrease in methane amounts in the inlet stream reduces the amount of H radical which promote the chemical decomposition of hydrogen sulfide, it also decreases methyl radical as well as other hydrocarbon radicals in the reaction pool which play an important role in the consumption of the produced sulfur or sulfurous species to form CS₂ that was shifting the equilibrium towards higher decomposition of hydrogen sulfide.

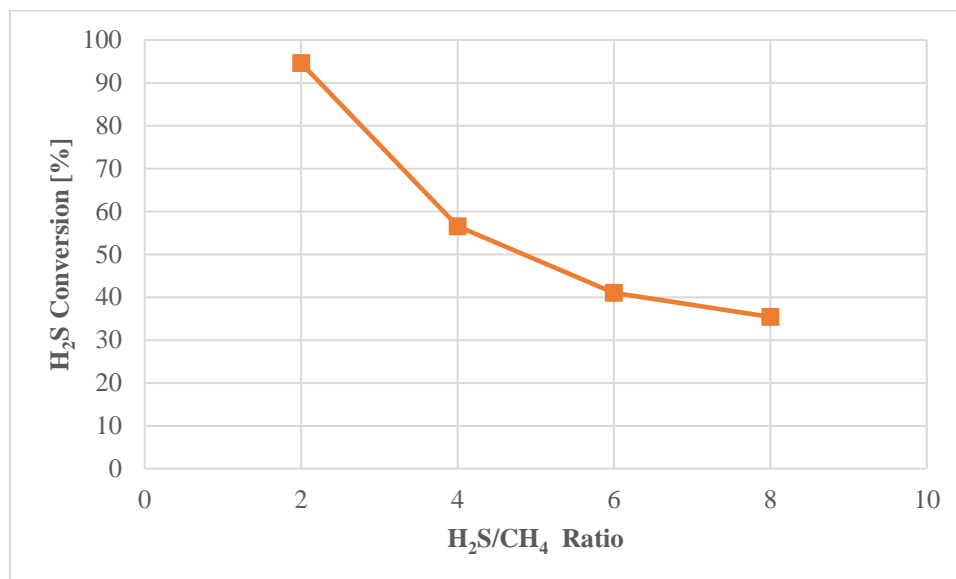


Figure 30. H₂S conversion as a function of H₂S/CH₄ ratio at temperature of 1573 K

Figure 31 shows the mole fraction of CS₂ formed with different H₂S/CH₄ ratio at reactor temperature of 1573 K. The formation of CS₂ also decreased with reduction in the methane amounts in the inlet stream. Recall that the formation of CS₂ occurs by the interaction between hydrocarbon radicals and sulfurous radicals or from the interaction between carbon and sulfur released. The limited hydrocarbon radicals or carbon provided to the reaction pool by the reduced methane amounts in the inlet stream reduces the amount of formed CS₂ in the products stream.

The other undesirable byproduct in this process is the carbon deposits. The carbon particles will deposit on the catalyst surface to poison the catalyst. Therefore, decreased deposition of carbon on the reactor surface gives an opportunity to prolong the life cycle of the catalyst. A slight decrease in CS₂ with the increase in the H₂S/CH₄ ratio from 2 to 4 shows that this increase in the hydrogen sulfide (or decrease in methane) concentration only increases the amounts of released sulfur that is required

to bond with formed carbon to result in the formation of CS_2 . This also means that the extra carbon formed with $\text{H}_2\text{S}/\text{CH}_4 = 2$ can be eliminated by reducing the methane concentration at inlet of the reactor.

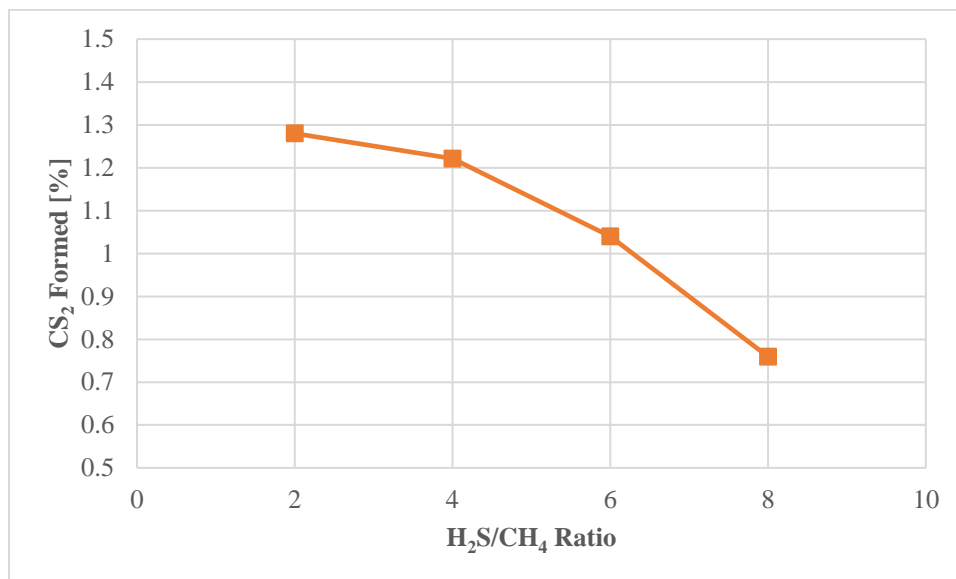


Figure 31. CS_2 mole fraction in the products stream as a function of $\text{H}_2\text{S}/\text{CH}_4$ ratio at temperature of 1573 K

4.2.3. Simulation and Validation of Hydrogen Production from Hydrogen Sulfide and Methane Mixture

Based on the positive results obtained on reformation of hydrogen sulfide to hydrogen with methane present, further investigation on the most dominant reaction pathways is provided in later section. The inlet composition was chosen to have minimal carbon formation that facilitates developing reaction mechanism simulating the experiment. Results on the H_2S reformation in the presence of CH_4 examined here are presented in the following. Results simulated numerically were also validated with the experimental data. The goal here was to quantify experimentally the speciation of H_2 from the reformation of CH_4 and H_2S over a range of temperatures at different

residence times and highlight the most dominant elementary reaction by simulating the reaction numerically.

Tay Yu Cong et al. [73] developed a detailed mechanism for the pyrolysis of hydrogen sulfide and validated with a wide assortment of experimental data as well as conditions available in literature. Detailed reaction mechanism of methane pyrolysis and combustion has been intrinsically developed and available [113]. Both mechanisms have been combined in addition to the reactions between hydrocarbons and sulfur from the literature [114] to build a full detailed mechanism for the pyrolysis of hydrogen sulfide in the presence of methane shown in Table 6. Carbon deposition is very difficult to model so that such reactions were not included in the mechanism and also the experimental conditions were chosen wherein carbon deposition was not favored. Very minor adjustment was made to the pre-exponential factor of some reaction to fit the experimental data. The detailed mechanism is presented in Table 6. Numerical simulations were performed using ChemKin Pro [115] code. A plug flow reactor model built in ChemKin Pro [115] software was used in the numerical simulation which was similar to that used in the experiments. The pressure was assumed constant in the plug flow reactor (PFR) and equal to the atmospheric pressure and that there were no heat losses.

Aspects of interest that will be investigated were amounts of hydrogen produced, reformation of H_2S and conversion of CH_4 . The parameters that will be studied experimentally were temperature and residence time while numerical simulations will provide knowledge on the most dominant elementary reactions in this treatment method. Generally, the interaction of hydrocarbons with sulfurous

compounds leads to the incidence of plentiful lateral reactions that promotes the formation of carbonaceous-sulfurous compounds. The presence of methane with hydrogen sulfide also leads to the formation of carbon disulfide (CS₂). However, this aspect was not the focus of this investigation. The effect of temperature on the production of hydrogen as well as conversion of hydrogen sulfide and residence time required to reach the asymptotic steady state condition were examined. This assisted to evaluate this treatment method for H₂S destruction as well as H₂ production. The result obtained on the amounts of hydrogen produced over the specified range of temperatures at different residence times are shown in Figure 32. In addition to the measurements, element balance was conducted to ensure consistency of the experimental data.

Table 6. Detailed mechanism of H₂S pyrolysis in the presence of CH₄ with the

$$\text{rate equation: } k = A \cdot T^b \cdot \exp(-E_a/(RT)) \text{ [32-34]}$$

REACTIONS	A [cm, mol, s]	b	E [$\frac{\text{cal}}{\text{mol}}$]
SH+CH ₃ =CH ₃ SH	9.998E+12	0.000	2969.67
SH+CH ₃ =CH ₂ S+H ₂	1.018E+15	0.000	0.000
H+CH ₃ SH=CH ₃ +H ₂ S	6.926E+12	0.000	1664.0
H + CH ₃ SH = CH ₃ S + H ₂	2.903E+12	0.000	2593.0
H + CH ₃ S = CH ₂ S + H ₂	1.988E+13	0.000	0.000
H + CH ₂ S = HCS + H ₂	5.252E+12	1.77	2989.29
H+HCS=CS+H ₂	1.211E+14	0.000	0.000
SH+CS=H+CS ₂	3.232E+10	1.50	495.0
CH ₄ +S=CH ₃ +SH	4.042E+14	0.000	19796.0
H ₂ S + M => SH+H+M	1.900E+15	0.000	64000
H ₂ S=SH+H	7.632E+04	0.000	82155.000
H ₂ S+M=S+H ₂ +M	1.600E+24	-2.610	89027.151
N ₂ /1.5/ SO ₂ /10/ H ₂ O/10/			
H ₂ S+H=SH+H ₂	1.20E+14	2.10	695.525
H ₂ S+S=>SH+SH	8.300E+13	0.000	2052.689
H ₂ S+S=H ₂ +S ₂	6.020E+12	0.000	4968.033
H ₂ S+S=HS ₂ +H	2.000E+13	0.000	7400.064
H ₂ S+S(+M)=H ₂ S ₂ (+M)	3.460E+12	0.200	-1432.000
Low pressure limit rate constant	LOW/		
Troe falloff parameters	TROE/		
N ₂ /1.3/			
H+H+H=H ₂ +H	3.200E+15	0.000	0.000
H+H+H ₂ =H ₂ +H ₂	9.790E+16	-0.600	0.000
H ₂ +M=H+H+M	4.580E+19	-1.400	104380.000
H ₂ O/1.2E1/ H ₂ /2.5/			
S+H+M=SH+M	6.200E+16	-0.600	0.000

S+H2=>SH+H	2.000E+14	0.000	76600.000
S+S+M=>S2+M	1.200E+17	-1.000	0.000
S2+M => 2S+M	4.800E+13	0.000	77103.872
S2+H+M=HS2+M	1.150E+25	-2.840	1665.000
duplicate			
S2+H+M=HS2+M	1.000E+16	0.000	0.000
N2/1.5/ SO2/10/ H2O/10/			
Duplicate			
SH+H=>H2+S	1.160E+18	0.000	21000.000
SH+S=S2+H	3.320E+12	0.500	-29.000
SH+SH=S2+H2	3.012E+14	0.000	0.000
SH+SH=>H2S+S	1.000E+14	0.000	430.000
SH+SH(+M)=H2S2(+M)	3.460E+12	0.200	-1432.000
Low pressure limit rate constant	LOW/	2.329E+31	-4.943
Troe falloff parameters	TROE/	1.000E+00	254.00
H2S2+M=>SH+SH+M	1.400E+15	1.000	57030.000
DUPLICATE			
HS2+H=SH+SH	1.100E+13	0.353	210.000
HS2+H=H2S+S	1.500E+08	1.551	2149.641
HS2+S=S2+SH	4.170E+06	2.200	-600.000
H2S2+H=HS2+H2	4.990E+03	1.933	-1408.000
H2S2+H=H2S+SH	2.000E+15	0.000	6000.000
H2S2+S=HS2+SH	2.850E+06	2.310	1204.000
HS2+H=S2+H2	1.200E+07	2.100	700.334
HS2+H+M=H2S2+M	1.000E+16	0.000	0.000
N2/1.5/ SO2/10/ H2O/10/			
SH+NH=SN+H2	1.000E+14	0.000	0.000
N+SH=SN+H	6.310E+11	0.500	8009.562
N+SN=N2+S	6.300E+11	0.500	0.000
S+NH=SH+N	1.000E+13	0.000	0.000
N2+M=N+N+M	1.000E+28	-3.300	225000.000
S+S2+M=S3+M	1.89E+15	0.000	-1788.000
S2+S2+M=S4+M	1.89E+15	0.000	-1788.000
S2+S3+M=S5+M	1.89E+15	0.000	-1788.000
S3+S3+M=S6+M	1.89E+15	0.000	-1788.000
S3+S4+M=S7+M	1.89E+15	0.000	-1788.000
S4+S4+M=S8+M	1.89E+15	0.000	-1788.000
H2+CH2(S)<=>CH3+H	7.23E+13	0.000	0.000
CH4+C<=>CH+CH3	5.00E+13	0.000	24015
CH4+H=>CH3+H2	7.94E+14	0.000	15154
CH4+CH<=>C2H4+H	3.01E+13	0.000	-396
CH4+CH2<=>CH3+CH3	4.30E+12	0.000	10038
CH4+CH2(S)<=>CH3+CH3	7.00E+13	0.000	0.000
CH4+C2H<=>CH3+C2H2	1.81E+12	0.000	0.000
C2H2+C2H2<=>H2CCCCCH+H	1.93E+09	0.000	57840
H2+C2H<=>C2H2+H	1.08E+13	0.000	2165
C+CH2<=>C2H+H	5.00E+13	0.000	0.000
C+CH3<=>C2H2+H	5.00E+13	0.000	0.000
H+CH<=>C+H2	8.37E+12	0.000	0.000
H+CH2<=>CH+H2	6.02E+12	0.000	-1780
H+CH2(S)<=>CH2+H	2.00E+14	0.000	0.000
H+CH3+M<=>CH4+M	6.00E+16	0.000	0.000
H+C2H3<=>C2H2+H2	1.20E+13	0.000	0.000
CH3+CH3<=>C2H5+H	1.80E+12	0.000	10400
CH+CH2<=>C2H2+H	4.00E+13	0.000	0.000
CH+CH3<=>C2H3+H	3.00E+13	0.000	0.000
CH+C2H3<=>CH2+C2H2	5.00E+13	0.000	0.000
CH2+CH2<=>C2H2+H2	1.20E+13	0.000	796
CH2+CH2<=>C2H2+H+H	1.08E+14	0.000	796
CH2+CH3<=>C2H4+H	4.22E+13	0.000	0.000
CH2+C2H3<=>C2H2+CH3	1.81E+13	0.000	0.000

CH₂(S)+M<=>CH₂+M	1.50E+13	0.000	0.000
CH₃+CH₃+M<=>C₂H₆+M	6.02E+17	-7.00	2763
CH₃+M<=>CH₂+H+M	2.37E+19	-2.17	0 ! R5
C₂H+C₂H₃<=>C₂H₂+C₂H₂	1.90E+13	0.000	0.000
H₂CCCCH+M<=>C₄H₂+H+M	1.12E+16	0.000	46510
C₂H₂+H+M<=>C₂H₃+M	5.70E-06	0.000	1470
C₂H₂+CH<=>C₂H+CH₂	2.11E+14	0.000	-172
C₂H₂+CH₂<=>C₃H₄	1.20E+13	0.000	6620
C₂H₂+CH₂(S)<=>H₂CCCH+H	3.00E+13	0.000	0.000
C₂H₂+C₂H<=>C₄H₂+H	8.97E+13	0.000	0.000
C₂H₂+M<=>C₂H+H+M	1.14E+17	0.000	106830
C₂H₄+H<=>C₂H₃+H₂	5.42E+14	0.000	14900
C₂H₄+H+M<=>C₂H₅+M	8.43E+08	1.49	1000
C₂H₄+CH<=>C₃H₄+H	1.32E+14	0.000	-344
C₂H₄+CH₂(S)+M<=>C₃H₆+M	9.64E+13	0.000	0.000
C₂H₄+CH₃<=>CH₄+C₂H₃	4.16E+12	0.000	11128
C₂H₄+M<=>C₂H₂+H₂+M	1.00E+17	0.000	71540
C₂H₄+M<=>C₂H₃+H+M	7.60E+17	0.000	96580
C₂H₆+H<=>C₂H₅+H₂	1.45E+09	0.000	7411
C₂H₆+CH<=>C₂H₄+CH₃	1.08E+14	0.000	-263
C₂H₆+CH₂(S)<=>CH₃+C₂H₅	2.40E+14	0.000	0.000
C₂H₆+CH₃<=>C₂H₅+CH₄	1.51E-07	6.00	6046

Simulation results agree favorably with the experimental data which allows determination of reaction pathways and the most dominant reactions. Both experimental and simulation results showed increased production of hydrogen with increase in reactor temperature. This increase was significant when the temperature exceeded 1373 K; at this temperature, methane (in the mixture with hydrogen sulfide) decomposed completely and all its hydrogen constituent were released, see Figure 33. Based on the qualitative agreement between the experimental data and the numerical simulation over the investigated operational conditions, reaction pathways and most dominant reactions could be identified. From the analysis of the reaction pathways, it was found that decomposition of methane occurred both thermally and chemically. Chemical decomposition of methane was dominated via reaction with active radicals, such as, H, S, SH. Methane thermal decomposition initiated with H-abstraction and methyl radical formation as expressed in reaction (46).



However, once reaction pool has been established to contain enough active radicals, chemical decomposition dominated the process via reactions (47, 48, 61). It has been observed that H radical as well as S radical accelerate the decomposition of methane and hydrogen sulfide chemically, see discussion here in the later section.



C₂ hydrocarbons have also been formed and they were detected experimentally but only in negligible trace quantities (two to three orders of magnitude smaller than hydrogen). The route for the formation of C₂ hydrocarbons is via recombination of methyl radicals but it is not significantly important under the studied conditions. The H-abstraction process that occurs to methane applies also to the C₂ bond hydrocarbon where these formed hydrocarbons decompose to C₂ hydrocarbon radicals and H radical. (see reactions 49-51).



Also, further decomposition of methyl radical along with H-abstraction increases the H, C and CH radicals in the reaction pool (52-55) along with the formation of H₂ (53-55).





Hydrogen molecule extracted from methane was dominantly obtained through the following reactions (47,49,51,53-55). It is important to note that although most of the possible routes for production of hydrogen and forming other hydrocarbons have been taken into consideration in the developed mechanism, reaction with methane has been found to be fastest and most dominated reaction in such a process.

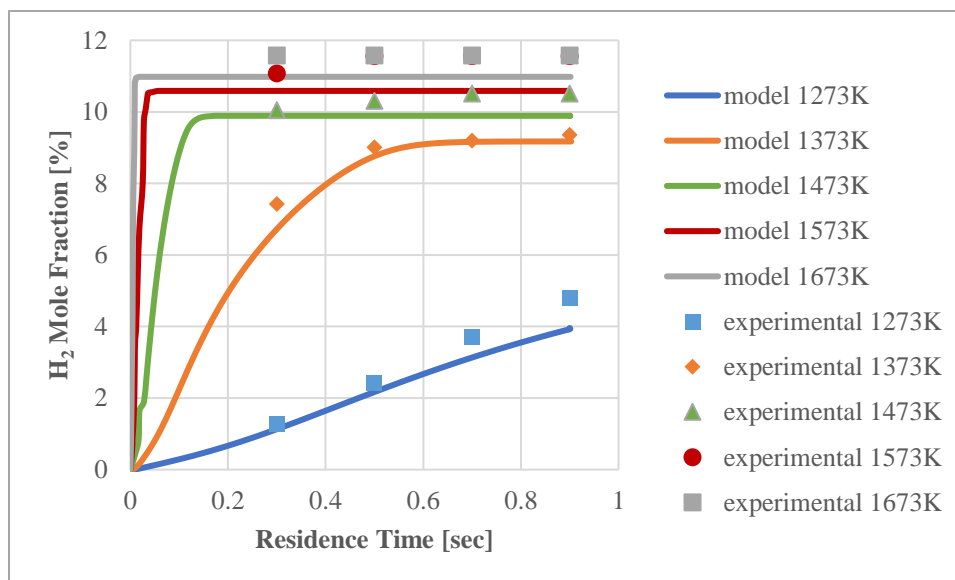


Figure 32. Effect of reactor temperature on the evolutionary behavior of hydrogen

The amounts of hydrogen produced continued to increase with increase in temperature at shorter residence times. After the complete conversion of methane, the hydrogen produced was at lower rate with respect to temperature which is attributed to the higher endothermicity of hydrogen sulfide decomposition. Also from Figure 32 and Figure 33, it can be deduced that the H_2 formed from CH_4 decomposition and consumption of H radical limited the positive effect associated with the chemical decomposition of hydrogen sulfide in the presence of methane. This point is further explained later.

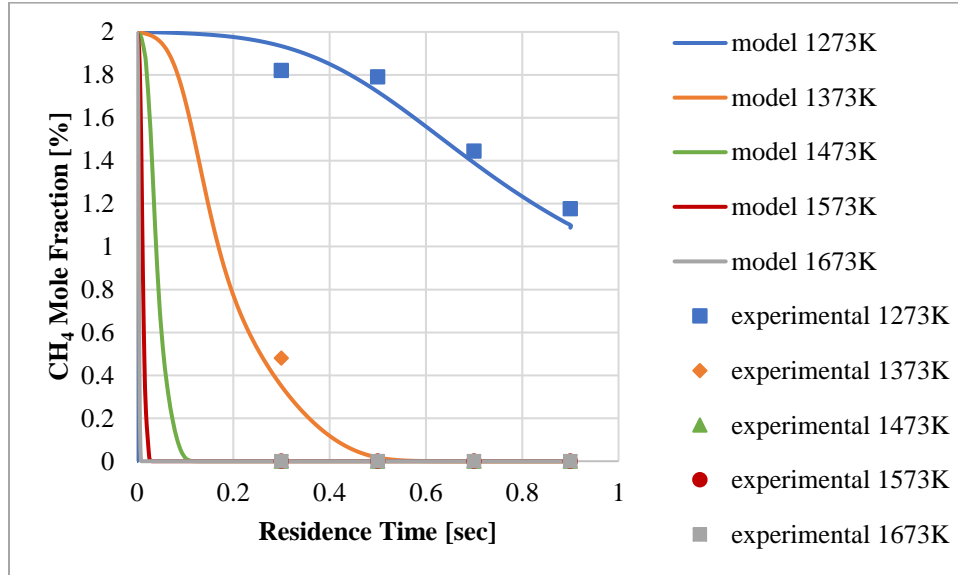


Figure 33. Temporal CH_4 consumption at different temperatures 1273-1673K

The results obtained on the evolutionary behavior of hydrogen sulfide conversion over a temperature range of 1273-1673K are shown in Figure 34. Thermal decomposition of hydrogen sulfide increased with increase in temperature and required shorter residence time to reach asymptotic steady state value, see Figure 34.

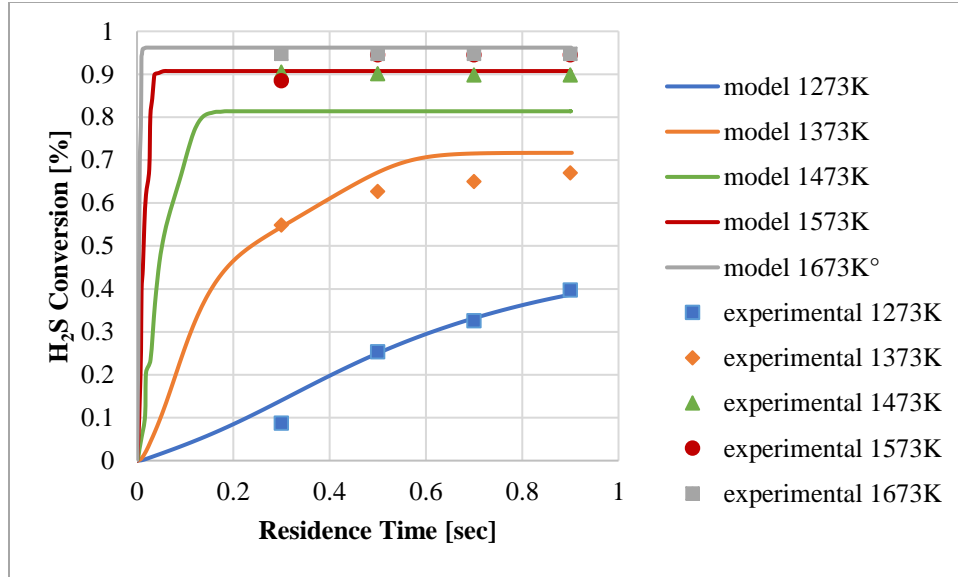


Figure 34. H₂S conversion as a function of temperature and residence time

The decomposition of hydrogen sulfide alone occurred both thermally via reactions (22-23) and chemically via reaction (24, 25, 56) producing S and H radicals. Numerical simulations conducted suggest that chemical decomposition of hydrogen sulfide is more dominant in the presence of abundant H-radical in the reaction pool. With more hydrogen radicals in the reaction pool due to decomposition of methane at relatively lower temperatures, conversion of hydrogen sulfide increased via chemical decomposition as shown in reaction (24). Karan and Behie [25] inferred that hydrogen radical reacts faster with hydrogen sulfide than methane, which supports that reaction (24) increases the consumption of hydrogen sulfide in the presence of methane.





Indeed, the amounts of hydrogen produced from the reformation of hydrogen sulfide with methane are due to the increased hydrogen feedstock in the inlet stream. A comparison between hydrogen produced from hydrogen sulfide decomposition alone and hydrogen sulfide reformation in presence of methane at residence time of 0.9 sec. was conducted and the results are depicted in Figure 35. The results show that at temperatures higher than 1350 K, hydrogen produced from the reformation of hydrogen sulfide in the presence of methane was higher than that produced from hydrogen sulfide alone as expected. Reasons behind this increase in amounts of hydrogen produced include: (a) increase in the hydrogen constituent feedstock in H₂S/CH₄ mixture, (b) relatively lower endothermicity of methane decomposition which liberates hydrogen at relatively lower temperature compared to hydrogen sulfide, (c) abundance of H-radical released associated with the presence of methane promotes the chemical decomposition of H₂S which may lead to high conversion rates of H₂S and finally (d) inevitable formation of CS₂ consumes one of the products of H₂S decomposition, which is S₂, and that in return shifts equilibrium towards more consumption of H₂S. The first two reasons are true but the other two reasons cannot be evaluated from the amounts of hydrogen produced. Consequently, a comparison between H₂S conversion in both cases was conducted to determine if the other two reasons were also true or not.

Conversion of hydrogen sulfide alone and also the reformation of hydrogen sulfide with presence of methane are shown in Figure 36. The results obtained ensure that conversion of hydrogen sulfide increased with the presence of methane and that equilibrium shift as well as the role H-radical was true. Based on the discussion and the

results obtained, this technique does not only extract more hydrogen from H_2S but also offers a more efficient treatment method than H_2S pyrolysis as it destructs more H_2S .

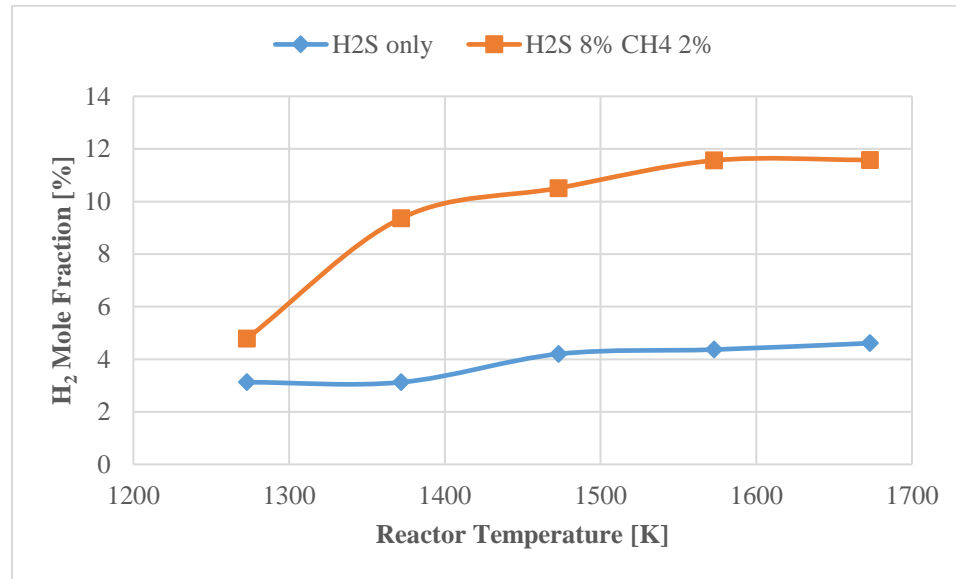


Figure 35. A comparison on the amounts of hydrogen produced from H_2S only and H_2S in the presence of CH_4

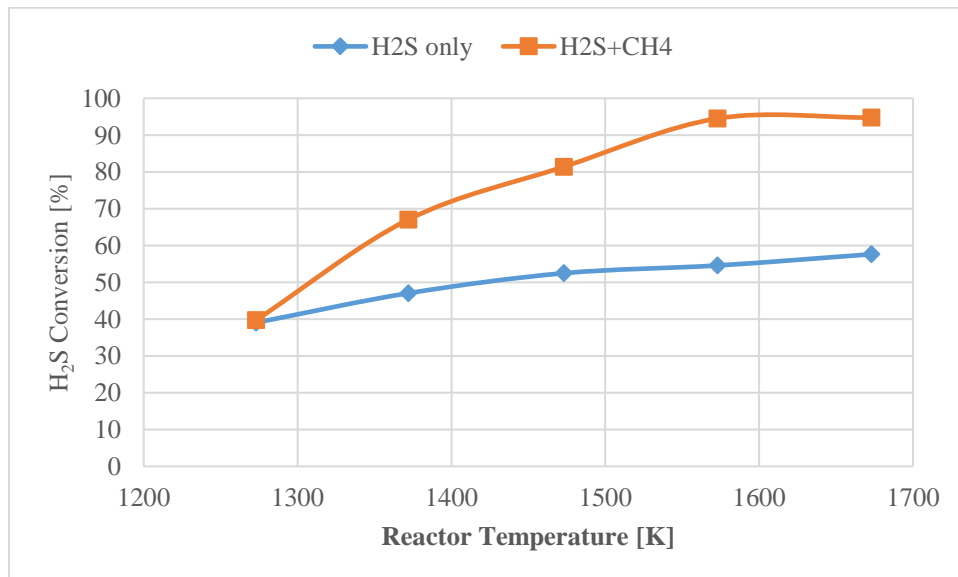


Figure 36. Comparison of H_2S conversion with H_2S only and $\text{H}_2\text{S}/\text{CH}_4$ mixture

4.2.3.1. Summary

Production of hydrogen from hydrogen sulfide reformation in presence of methane has been examined numerically and experimentally using a plug flow reactor. The results showed superior performance to decompose hydrogen sulfide and produce clean hydrogen. The effect of reactor temperature and $\text{H}_2\text{S}/\text{CH}_4$ mixture ratio on the production of hydrogen as well as the formation of carbon disulfide was examined over a temperature range of 1273–1673 K at different residence times in the reactor. The results revealed the direct role of methane accompanying H_2S on the amounts of hydrogen produced during the reformation of hydrogen sulfide. Presence of methane in the H_2S gas stream enhanced the conversion of hydrogen sulfide and increased the amount of hydrogen produced while forming CS_2 and carbon deposits on reactor surface. The operational conditions at which carbon deposits were minimum are highlighted. However, CS_2 was also formed that can be used as a feedstock in the contemporary Claus process. Enhanced destruction of hydrogen sulfide occurred in the presence of methane. As much as 95% hydrogen recovery has been demonstrated experimentally from a mixture of hydrogen sulfide and methane. Increase in temperature to 1373 K shortened dramatically the residence time required to reach the asymptotic steady state composition along with significantly increased amounts of hydrogen as compared to that obtained from H_2S alone. The qualitative agreement between the experimental data and the simulations results revealed the validity of the mechanism to identify the dominant reaction pathways. Alternatively, the treatment of hydrogen sulfide rich sub-quality natural gas to hydrogen is also well suited so to avoid the required separation of hydrogen sulfide from the natural gas prior to the treatment.

The presence of impurities, such as hydrocarbons is expected to further enhance the production of hydrogen but it is expected to increase the formation of carbon disulfide as well as carbon.

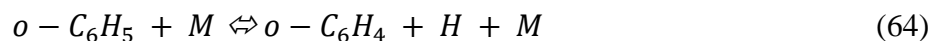
4.2.4. Reformation of Hydrogen Sulfide to Hydrogen in Presence of Benzene

Other impurities that are naturally accompanying separated hydrogen sulfide stream are benzene, toluene and benzene commonly called BTX. Reformation of hydrogen sulfide in the presence of benzene were examined and the results are presented here with the objective of experimental quantification on the amounts of hydrogen produced and hydrogen sulfide destructured over the range of temperatures and inlet stream composition.

4.2.4.1. Effect of Reactor Temperature on Reformation of H₂S with C₆H₆ Present

Reformation of hydrogen sulfide in the presence of benzene was examined over range of temperatures of 1273-1573 K using a quartz tubular reactor at comparatively long residence time of 1 second. The effect of reactor temperature on the conversion of hydrogen sulfide and amounts of hydrogen produced was examined. The results were obtained from 9.23% H₂S / 0.77% C₆H₆ / 90% N₂ mixture, which reflects the H₂S/C₆H₆ stoichiometric ratio of 12 in reaction between hydrogen sulfide and benzene since N₂ was inert. The amounts of C₆H₆ in the mixture are relatively high compared to its composition practically. However, stoichiometry was used as base case for 2 reasons: first reason being higher composition of C₆H₆ have measurable impact compared to

low concentrations; second reason being taking stoichiometry as reference facilitates comparison with other HC's. Results on the amounts of hydrogen produced over the different temperatures examined are depicted in Figure 37. Hydrogen was observed to increase with increase in reactor temperature. Quantification of the remaining benzene in the products stream was not possible since benzene is liquid at room temperature and vapors are condensed before sample being analyzed by the GC. However, an indication of presence of benzene or complete destruction of benzene could be obtained using FID detector with bounded detection limits. The results obtained showed no hydrocarbons at temperatures higher than 1373 K. This reveals that benzene has less thermal stability compared to hydrogen sulfide. Consequently, thermal decomposition of benzene initiated thermally via unimolecular dissociation reaction (62) at first and continued to decompose thermally in the same time it decomposes chemically via bimolecular reaction (63) with the active radicals such as H radical as well as other hydrocarbon radicals. The produced H radical provided important role in fostering benzene and hydrogen sulfide chemical decomposition as discussed in later section. Thermal decomposition initiated by extraction of H-atom rather than breaking C-C bond and opening the ring which enriches the reaction pool with active H radical. Further dissociation of benzene as well as formed hydrocarbons to carbon and gases was the most favorable route at this range of temperatures with most of the gases being hydrogen except few others with concentration in hundreds of ppm's.





Where o – symbol refers to the aromatic ring and l – symbol refers to linear chain.

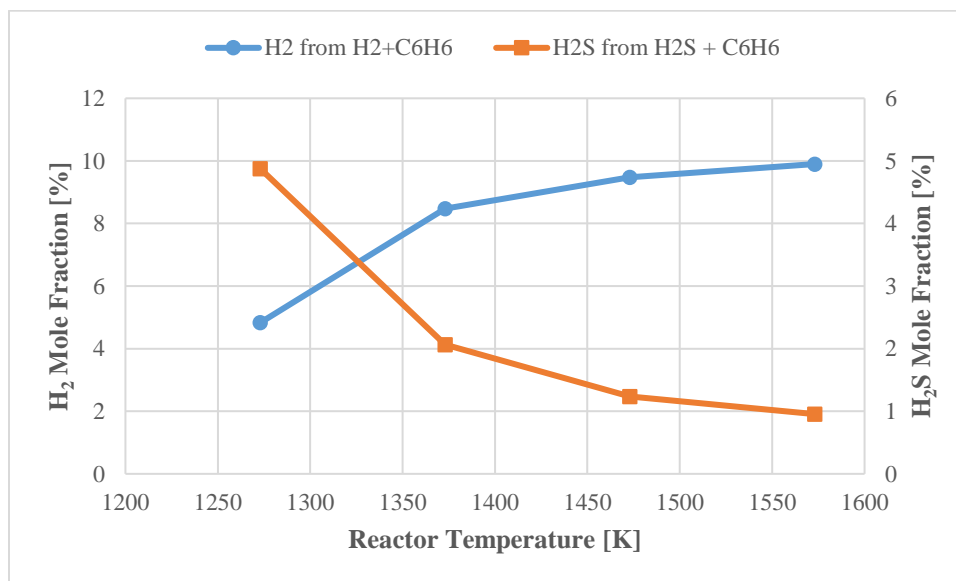


Figure 37. Effect of reactor temperature on hydrogen production

The presence of hydrocarbon-benzene in the thermal dissociation of hydrogen sulfide provided interaction between hydrocarbon and sulfurous radicals at very high probability as well as to promote the formation of carbonaceous-sulfurous compounds, carbon disulfide in this case. Under the examined conditions, carbon disulfide was not the only carbon-constituted compound formed; the carbon itself deposited on the inner surface of the reactor. Given the complete conversion of benzene at temperatures higher than 1373 and the observed carbon deposit at all temperatures, one can infer that the formation of carbon disulfide is limited by hydrogen sulfide thermal decomposition which supports the findings of Chin et al. [112] and Karan and Behie [79].

Composition of carbon disulfide evolved from the stoichiometric $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ mixture at different temperatures ranging from 1273-1573 K and at residence time of 1 sec is shown in Figure 38. Carbon disulfide was observed to increase with increase in temperature. Since formation of carbon disulfide is limited by thermal dissociation of hydrogen sulfide, increased hydrogen sulfide dissociation at high temperatures provided sulfurous species to the reaction pool to further promote the formation of carbon disulfide. This resulted in increased carbon disulfide composition in products stream with increase in temperature.

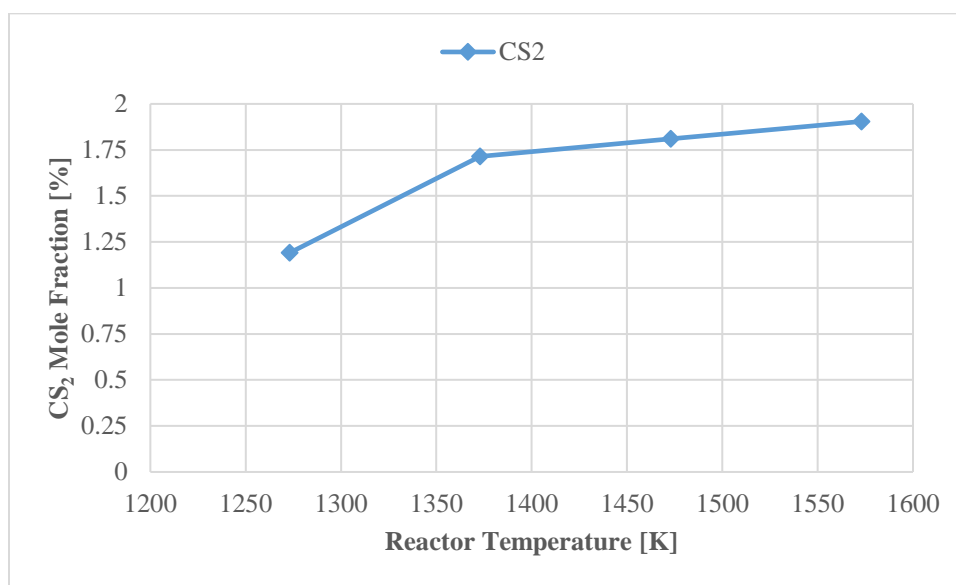
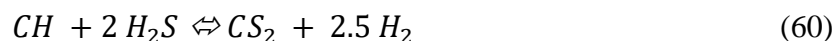


Figure 38. Effect of reactor temperature on CS_2 formation

Possible routes for interaction between carbonaceous radicals and sulfurous radicals for carbon disulfide formation are:



4.2.4.2. Effect of C_6H_6 Presence on Reformation of H_2S

Since a mixture of hydrogen sulfide and benzene (C_6H_6) has higher H_2 feedstock, presence of benzene was expected to increase the amounts of H_2 produced. To quantify the upsurge in hydrogen production, a comparison between amounts of hydrogen produced with and without benzene present in the reactant stream was made. In both cases, the composition of hydrogen sulfide remained the same to eliminate the effect of difference amounts of H_2S concentration. The comparison between the amounts of hydrogen produced is depicted in Figure 39. Enhanced hydrogen production with benzene present can be observed even at the lowest temperature examined. The complete conversion of benzene was identified from the absence of any benzene trace detected with the FID at any temperature other than 1273 K.

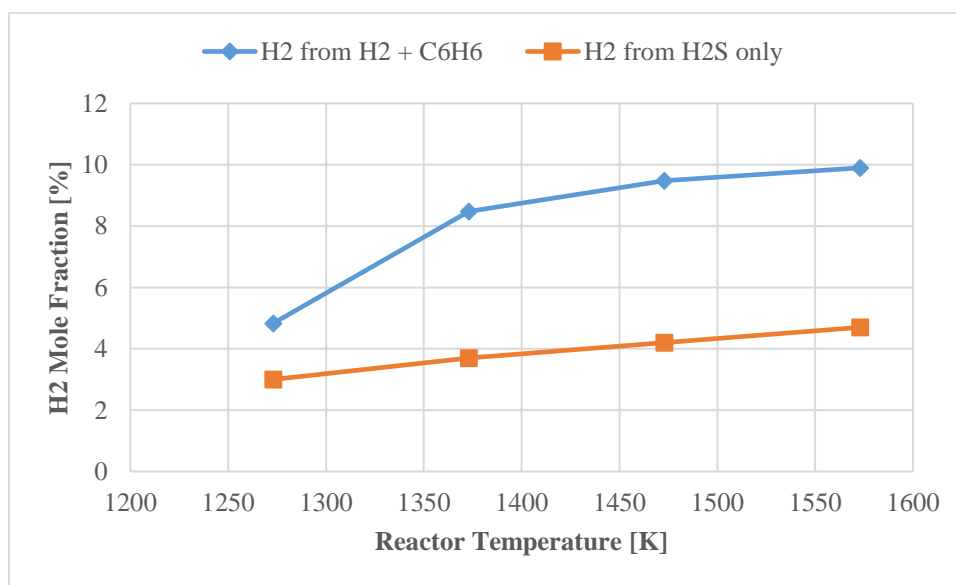


Figure 39. H_2 produced from hydrogen sulfide with benzene and H_2S only

From quantification on gain in hydrogen production from hydrogen sulfide stream in the presence of benzene, one can conjecture that this technology could be used for the treatment of hydrogen sulfide. To evaluate this further, the effect of

presence of benzene on hydrogen sulfide destruction must be isolated and quantified regardless of the increased hydrogen production. The comparison reveals one of three possibilities. First being that the increase in hydrogen production is due to the increased hydrogen in feedstock. However, the benzene hindered hydrogen sulfide conversion. Second being that enhanced hydrogen production achieved in the presence of benzene was due to simultaneous decomposition of hydrogen sulfide and benzene while presence of benzene did not affect hydrogen sulfide conversion. Last one being that hydrogen production increased due to increased hydrogen feedstock in the $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ mixture as well as increased hydrogen sulfide conversion. Figure 40 provides a comparison on the conversion of hydrogen sulfide in both cases given above and depicts that the last possibility of higher H_2 feedstock in inlet and higher conversion of H_2S is valid. The presence of benzene not only increased hydrogen feedstock in the inlet stream but also fostered destruction of hydrogen sulfide which reveals enhanced potential of this method as a treatment method of hydrogen sulfide stream. The increased conversion of hydrogen sulfide can be viewed from two different perspectives of thermodynamic and kinetic. Thermal dissociation of hydrogens sulfide is known to suffer from the chemical equilibrium limitation due to backward reactions between hydrogen and sulfur to form hydrogen sulfide. However, in presence of benzene, one of the main products of hydrogen sulfide dissociation is devoted for the inevitable formation of carbon disulfide. This consumption of sulfur relocates the equilibrium limit forward for higher hydrogens sulfide conversion to amend for sulfur consumption. This supports enhanced destruction of hydrogen sulfide in the presence of benzene to be thermodynamically favored. Kinetically, thermal dissociation of

hydrogen sulfide alone is initiated thermally via unimolecular decomposition reactions (22-23) producing H, S and SH radicals. After the radical pool becomes established the dissociation continues to occur thermally as well as chemically via bimolecular reactions with H, S and SH radicals wherein more hydrogen sulfide is destroyed in favor of producing more radicals that either consumes more hydrogen sulfide or reacts to form the end products of either hydrogen or sulfur, see reactions (24, 25, 56).

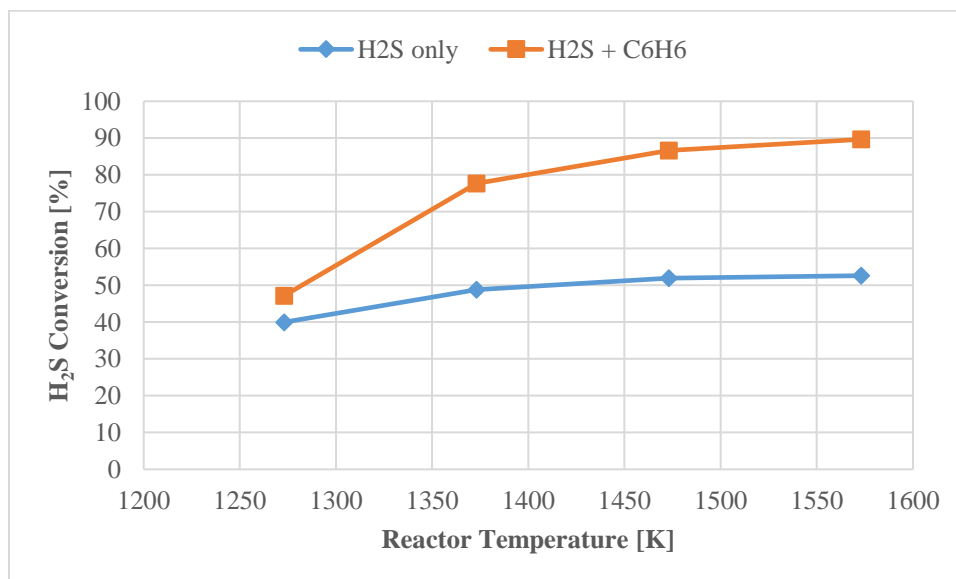
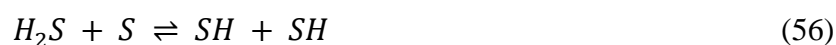
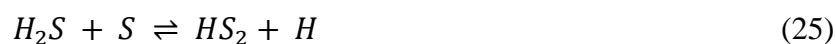
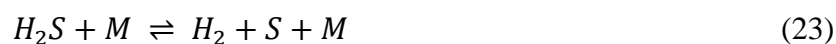


Figure 40. H₂S conversion as a function of temperature for 9.23% H₂S/0.77% C₆H₆ in 90% N₂ and 9.23% H₂S in 90.77% N₂ mixtures

Since presence of benzene increased hydrogen feedstock in the inlet stream, it then increased the hydrogen radicals during course of the reaction at these temperatures to increase the reaction route (24) leading to higher hydrogen sulfide conversion.

4.2.4.3. Effect of C₆H₆ Composition on H₂S Reformation

At the stoichiometric ratio of H₂S/C₆H₆ which corresponds to the inlet stream composition of 9.23% H₂S / 0.77% C₆H₆ / 90% N₂, carbon deposits could be visually observed on the inner surface of the reactor at all the temperatures examined. Due to the comparatively lower thermal stability of benzene which lead to complete decomposition at temperatures lower than those required for complete conversion of hydrogen sulfide, the main products of benzene dissociation were carbon, hydrogen and hydrocarbon radicals. However, at the same temperature incomplete dissociation of hydrogen sulfide makes the reaction pool to lack sulfur and sulfurous radicals for reaction with the products from benzene dissociation. This relative scarcity of sulfur to form carbon disulfide blocks routes for carbon consumption other than forming solid carbon deposits. The problem associated with carbon deposits tends to appear while accelerating the dissociation reaction using catalysts. This carbon deposits can poison the catalyst by significantly reducing the active surface area. In order to eliminate carbon deposits in the reactor, two intuitive routes can be taken. First route is to achieve higher hydrogen sulfide dissociation rate to produce enough sulfur and sulfurous radicals to react with formed carbon and hydrocarbon radicals and form carbon disulfide. To estimate the relative rate at which hydrogen disulfide gets dissociated, formation of carbon disulfide molecule will require 12 molecules of hydrogen sulfide and 1 molecule of benzene for stoichiometric conditions. Given this stoichiometry,

decomposing hydrogen sulfide at a rate 12 times faster than benzene is impractical with the equilibrium limitations and high endothermicity of hydrogen sulfide compared to benzene. However, due to the enhanced destruction of hydrogen sulfide in the presence of benzene, the factor of relative rates of decomposition of 12 may be excessive. The other route of eliminating carbon deposits on the reactor is to reduce the amounts of carbon content introduced to the reaction pool by increasing $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratio, which excludes the redundant carbon that leads to carbon deposits other than to react and form carbon disulfide. Consequently, different $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratios were examined in the same reactor at the same residence time of 1 second at constant temperature of 1473 K for all the $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratios. $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratio of 12 that reflects stoichiometry also represented the baseline case for this comparison. Other ratios of 18 and 24 were examined that represents 1.5 and 2 times the stoichiometry ratio values. This mixture was kept 10% in all cases with the remaining being nitrogen. The objective here was to attempt elimination of carbon deposits and quantify the reduction in carbon disulfide formation from reduction in benzene composition. Also, the impact of reducing composition of benzene in the mixture was explored to determine the amounts of hydrogen produced and hydrogen sulfide destructed. The results on the hydrogen produced from different mixtures ratios as well as remaining undecomposed hydrogen sulfide are shown in Figure 41. Amounts of hydrogen produced were observed to decrease with increase in $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratio. This decrease pertains to reduced hydrogen constituent from the decrease in benzene composition in the mixture. However, it can also be related to lower conversion of hydrogen sulfide. Figure 41 also shows increased amounts of hydrogen sulfide remaining in the products stream, which can be from two

reasons of increased hydrogen sulfide concentration in the inlet stream or lower conversion of hydrogen sulfide due to lower composition of benzene in the mixture. However, from the given inlet composition in the respective cases and increased hydrogen sulfide amounts remaining in the products stream, it can be conjectured that the conversion of hydrogen sulfide was reduced.

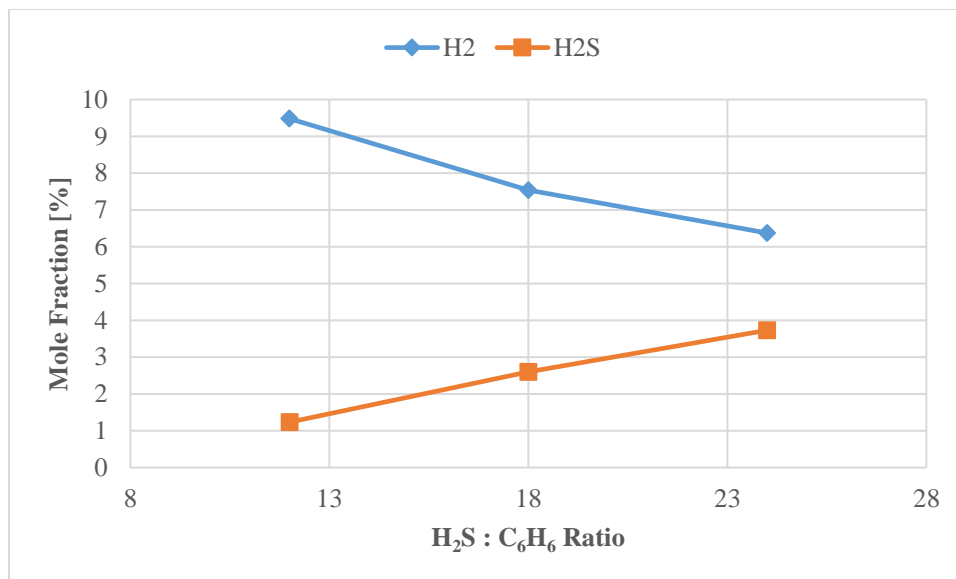


Figure 41. H₂ and H₂S with change in H₂S/C₆H₆ ratio (H₂S/C₆H₆ diluted in 90% N₂)

The results on the decreased conversion of hydrogen sulfide due to decrease in benzene amounts in the inlet stream is shown in Figure 42. Since the decrease in the conversion of hydrogen sulfide is strongly related to the less amounts of benzene present in the mixture, this can be attributed to the comparatively lower amounts of H radical introduced to the reaction pool by benzene decomposition. The reduced amounts of H-radical in the reaction pool impacts the chemical decomposition of hydrogen sulfide to cause an increase in hydrogen sulfide amounts in the products stream. Also, less benzene in the inlet stream limits the carbon constituent required for CS₂ formation. Although, formation of CS₂ is undesirable, it consumes sulfur and shifts

equilibrium towards more consumption of hydrogen sulfide. Lower carbon constituent reduces consumption of sulfur to form CS_2 , which get the equilibrium limit back again closer to the equilibrium limit of thermal dissociation of hydrogen sulfide alone.

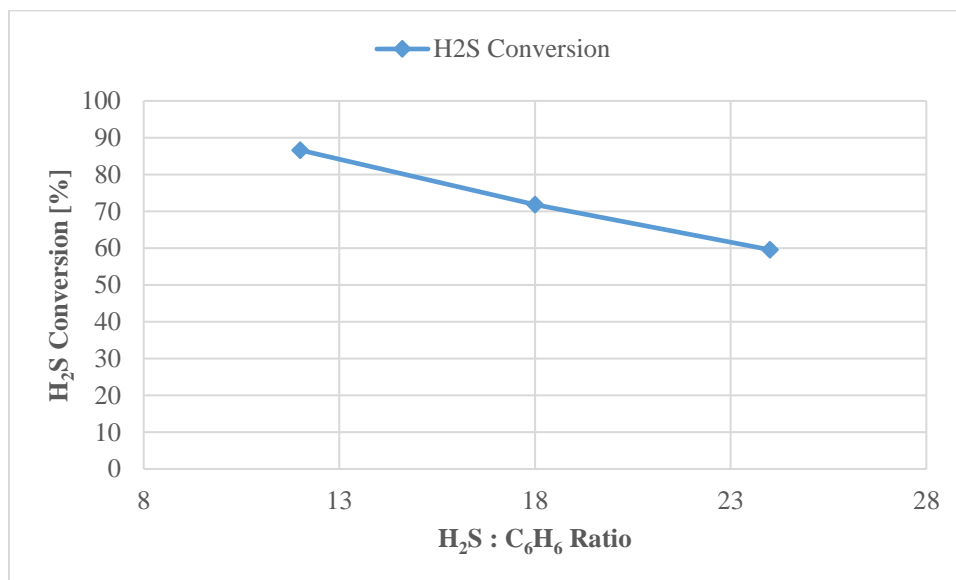


Figure 42. H₂S conversion as a function of H₂S/C₆H₆ ratio at temperature of 1473 K

The molar percentage of formed CS_2 is expected to be affected by reduction in carbon constituent introduced to the reactor since the composition of benzene in inlet stream was decreased. Figure 43 shows composition of formed CS_2 in the products stream at reactor temperature of 1473 but at different H₂S/C₆H₆ ratios. Formation of CS_2 was limited by the interaction between hydrocarbon and sulfurous radicals. The redundant carbon constituent was reduced by increasing H₂S/C₆H₆ ratio causing carbon-constituted species to decrease that interacts to form CS_2 . This subsequently leads to the decrease of CS_2 as shown in Figure 43.

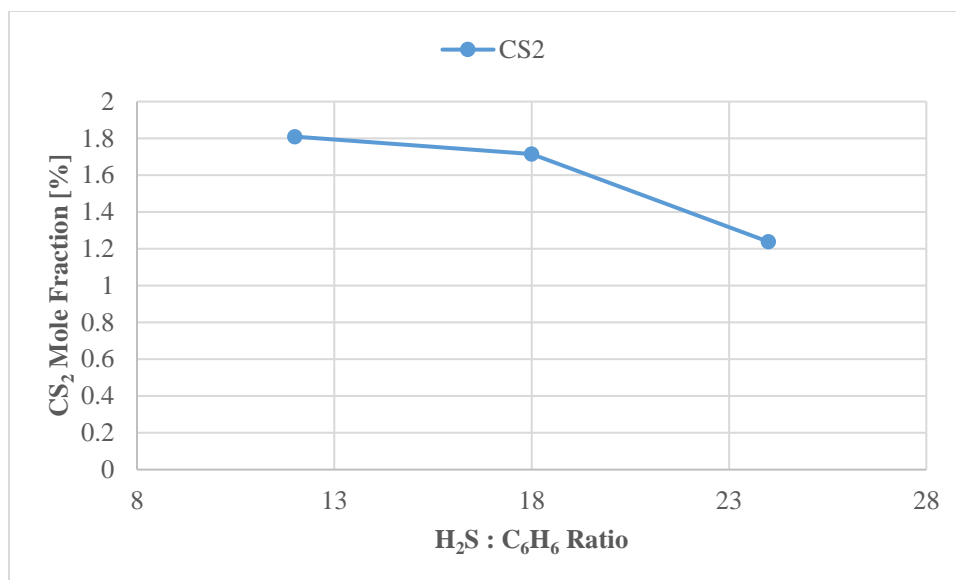


Figure 43. CS₂ mole fraction in the products stream as a function of H₂S/C₆H₆ ratio at temperature of 1473 K

Although CS₂ is undesirable byproduct of this reformation process, its separation from the products stream can be achieved in a multistage condensation system followed by absorption in mineral oil. The other undesirable product of this process is carbon in the form of carbon deposits. The reason that this product is undesirable in the process is that it can deposit on the catalyst to decelerate the reaction and may also result in pore mouth poisoning that adversely affects the catalytically active area of active sites. Thus, eliminating carbon deposition gives an opportunity to prolong catalyst life cycle in the reformation process. The quantification of carbon deposits was cumbersome so that only visual observations have been reported here. Carbon deposits were observed at all examined temperatures and stoichiometric ratios. It was visually observed to decrease significantly with increase in H₂S/C₆H₆ ratio to 18. For carbon deposits to be observed at this ratio, longer times allowed during experimentation assisted for seeking such a condition. And it took even longer to

observe carbon at the highest ratio. However, based on carbon element balance between reactants and products there has been carbon deposition even at the highest ratio. Protracted use of reactor under the highest ratio condition showed minimal carbon deposition on the reactor surface or in the sampling probe at the highest ratio. This points out that the carbon deposition was in the early stage where benzene reach its decomposition temperature before H_2S starts breaking down. Given the practical presence of BTX in hydrogen sulfide stream and results obtained under defined conditions, carbon deposition is minimal to occur at low temperatures ($\sim 1473\text{ K}$).

4.2.4.4. Summary

Experimental data on hydrogen production via thermal reformation of hydrogen sulfide in presence of benzene have been reported here. Effect of reactor temperature in range of 1273-1573K as well as $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ ratio in inlet stream at relatively long residence time was examined. These operational parameters were found to directly affect the amounts of hydrogen produced, hydrogen sulfide destructed and carbon disulfide formed. The role played by presence of benzene was established by comparing the amounts of hydrogen produced from hydrogen sulfide with or without the presence of benzene in the H_2S . Another comparison was also made between hydrogen sulfide destruction in both cases of without and with benzene. The results revealed enhanced destruction of hydrogen sulfide as well as more hydrogen production from hydrogen sulfide in case of presence of benzene. The results showed significant effect of reactor temperature along with increased production of hydrogen and hydrogen sulfide conversion at increased reactor temperatures. At higher reactor temperatures, the formation of carbon disulfide increased. $\text{H}_2\text{S}/\text{C}_6\text{H}_6$ mixture

composition was an important parameter that affects the amounts of carbon disulfide formed as well as the carbon deposition on reactor surface. The results showed that presence of benzene is beneficial for thermal reformation of hydrogen sulfide as an innovative treatment technology of hydrogen sulfide stream with no adverse impact on treatment process on its performance, unlike that observed in Claus reactors.

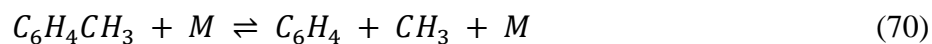
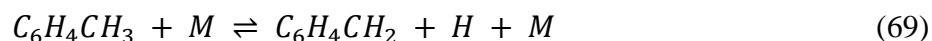
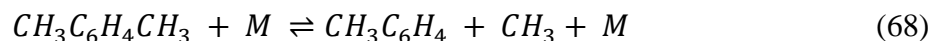
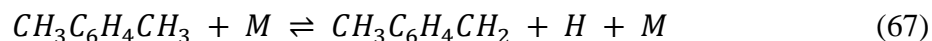
4.2.5. Reformation of Hydrogen Sulfide to Hydrogen with Xylene Present

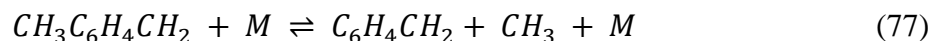
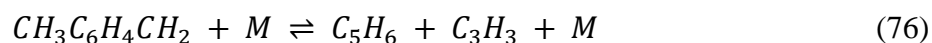
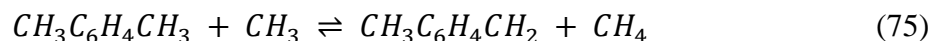
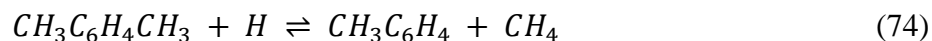
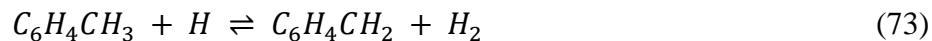
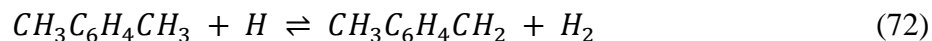
Results on the reformation of H_2S in the presence of C_8H_{10} were examined and are presented here in the following. The speciation of H_2 was quantified experimentally from simultaneous reformation of H_2S and C_8H_{10} over a range of temperatures and different inlet compositions. The amounts of CS_2 formed was quantified under examined conditions as well as the occurrence of carbon deposition on reactor walls.

4.2.5.1. Effect of Reactor Temperature on H_2S Reformation with C_8H_{10}

Reformation of hydrogen sulfide in the presence of xylene was examined over a temperature range of 1273-1573K using the quartz plug flow reactor at a relatively long residence time of 1s. Composition of the inlet stream to the reactor was 10% of $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ mixture and 90% of inert N_2 diluent. The $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ composition ratio was 16. This ratio was chosen to seek stoichiometric conditions for the global reaction since N_2 is inert. Effect of reactor temperature on hydrogen production, hydrogen sulfide destruction as well as formation of CS_2 was investigated. Figure 44 shows the results on the amounts of hydrogen produced at different temperatures. It can be observed that

the amounts of hydrogen increased monotonically with increase in temperature. Note that the results shown here are based on sulfur free stream. Xylene decomposition initiated thermally and it continued to occur thermally as well as chemically via active radicals. Xylene thermal decomposition initiation has more than one route, either by extraction of one of the methyl groups or H-abstraction from one of the attached methyl groups via unimolecular dissociation reactions (67-71). Once radicals such as H, CH₃ as well as other hydrocarbon radicals from the thermal dissociation are released, chemical decomposition of xylene occurs via radical bimolecular reactions given in reactions (72-75). Further decomposition from higher hydrocarbon to low hydrocarbons continued via thermal and chemical decomposition, such as reactions (76, 77). Recombination of methyl groups to form C₂ hydrocarbons, formation of methane or formation of lower hydrocarbons from higher hydrocarbon decomposition were also available routes. Further decomposition of lower hydrocarbon formed released more H-radical to the reaction pool. However, these can be intermediate routes as formation of hydrocarbon was not favored at such elevated temperatures. C₁-C₃ hydrocarbons were detected in very small quantities (ppm levels). The amounts of detected C₁-C₃ hydrocarbons were 3-4 orders of magnitude less than the other major products, and hence they were not reported.





Production of hydrogen increased significantly when the temperature exceeded 1373 K due to the release of hydrogen from the complete decomposition of xylene above this temperature.

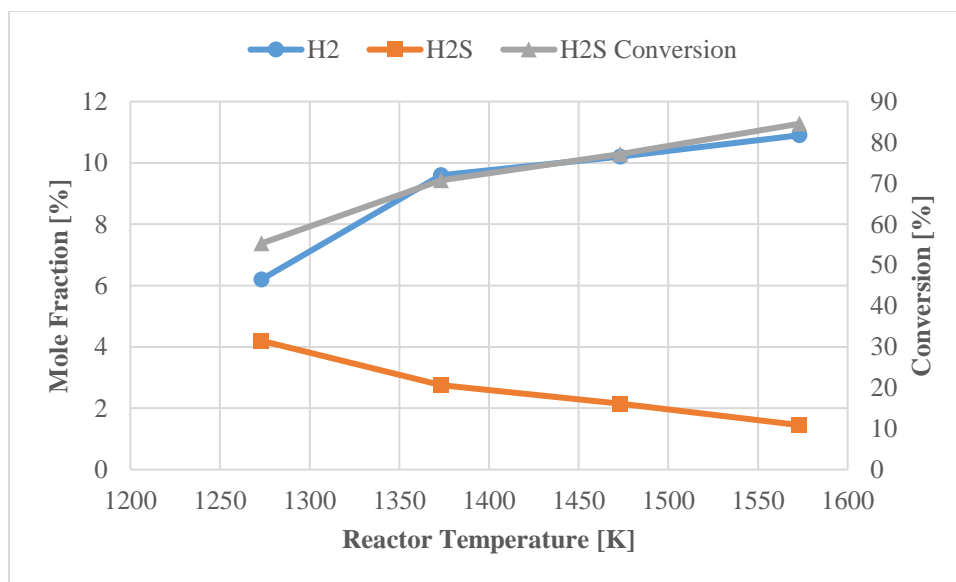


Figure 44. Effect of reactor temperature on hydrogen production from hydrogen sulfide and xylene mixture

In general, presence of sulfurous and carbonaceous compounds and radicals in the same reaction pool leads to the occurrence of ample lateral reactions which results in formation of sulfurous–carbonaceous compounds. In the present experiments, reactions between hydrogen sulfide and xylene and their derived radicals fostered the

formation of CS₂. However, carbon deposition observed visually under the studied conditions suggests that xylene dissociation was faster than dissociation of hydrogen sulfide. Thus, limiting step on the rate of formation of CS₂ was hydrogen sulfide dissociation. This finding agrees well with the results and observations of Chin et al. [112], and also Karan and Behie [79].

The CS₂ evolved from H₂S/C₈H₁₀ mixture at different temperatures in the range of 1273-1573 K and at residence time of 1s is shown in Figure 45.

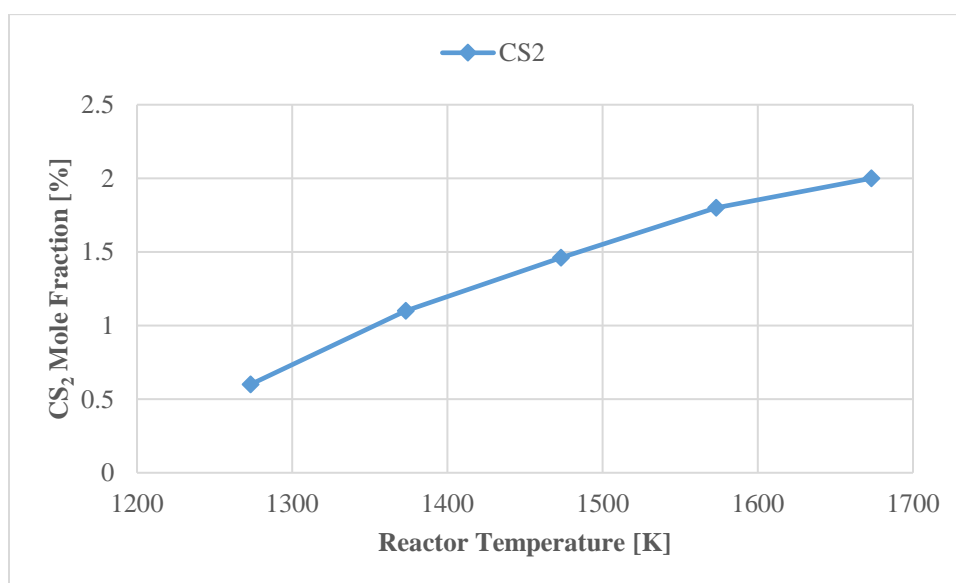


Figure 45. Effect of reactor temperature on CS₂ formation from hydrogen sulfide and xylene mixture

Since, the formation of CS₂ is attributed to the interaction of xylene-derived species and radicals with sulfur species, possible channels for formation of CS₂ are numerous; some of the chemical reactions (78-81, 58-60) are given below:





Formation of CS₂ was unavoidable over the whole range of temperature of 1273-1573K due to the presence of xylene and relative abundance in carbonaceous radicals and compounds along with sulfur species liberated from hydrogen sulfide. Increased formation of CS₂ with increase in temperature was expected due to higher conversion of hydrogen sulfide achieved which provided increased availability of sulfur species to react and form CS₂. It also supports the inference that dissociation of H₂S was the limiting step of CS₂ formation.

4.2.5.2. Effect of Xylene Presence on Reformation of H₂S

In order to evaluate the role played by xylene in the reformation of H₂S, a comparison was made between the amounts of hydrogen produced from H₂S stream diluted in N₂ and a mixture of H₂S and C₈H₁₀. The concentration of H₂S in both the streams was the same so that the effect of H₂S concentration was eliminated. Since the H₂S/C₈H₁₀ is richer in hydrogen constituent than hydrogen sulfide alone, increased production of hydrogen with xylene present was expected. This comparison was beneficial for two reasons. First it quantified the gain in hydrogen production when C₈H₁₀ was present. Second, it substantiated the effect of presence of xylene on hydrogen sulfide destruction. Figure 46 depicts that the amounts of hydrogen produced from H₂S/C₈H₁₀ mixture was higher (more than 40%) than that produced from thermal decomposition of hydrogen sulfide over the whole range of temperatures examined.

Figure 46 also shows the change of slope of the curve representing the amounts of hydrogen produced from $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ mixture that indicates early liberation of hydrogen constituent in xylene at relatively lower temperature compared to hydrogen sulfide. This can be attributed to the relatively lower thermal stability and lower endothermicity of xylene compared to hydrogen sulfide.

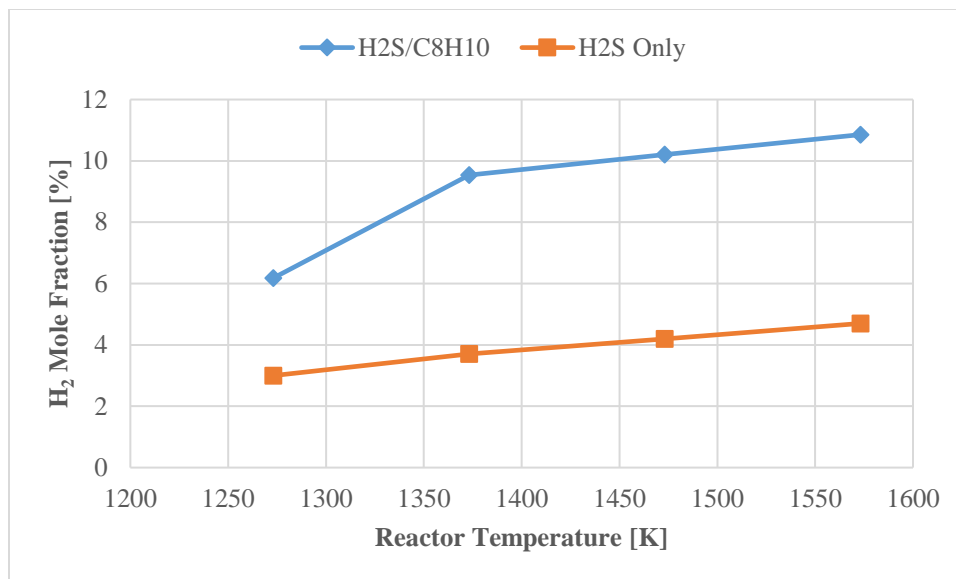


Figure 46. Hydrogen produced from hydrogen sulfide with xylene and hydrogen sulfide only

The results showed that the presence of xylene increased the amounts of hydrogen extracted from hydrogen sulfide. In order to evaluate reformation of hydrogen sulfide in the presence of xylene as a treatment method of hydrogen sulfide, comparison between hydrogen sulfide conversions using $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ mixture or H_2S alone was made, see Figure 47. Results showed that indeed hydrogen sulfide conversion increased in the presence of xylene. The increased hydrogen sulfide conversion in the presence of xylene can be attributed to two reasons. First, the equilibrium limit on thermal dissociation of hydrogen sulfide due to reverse reactions

between recovered sulfur and produced hydrogen shifted towards hydrogen sulfide destruction. This equilibrium shift is caused by the fact that sulfur and sulfurous radicals are consumed to form CS₂ from the presence of xylene. Consumption of one of the main products of H₂S thermal decomposition reaction moves the equilibrium towards further H₂S consumption. Therefore, higher H₂S destruction is thermodynamically favored. Furthermore, decomposition of hydrogen sulfide was initiated thermally via unimolecular reactions (22-23) producing H, SH and S radicals. Thermal decomposition continues to occur along with chemical decomposition via bimolecular reaction with H, S, SH radicals, as well as other hydrocarbon radicals from xylene decomposition. Accordingly, additional hydrogen sulfide consumption can occur via the following reactions:



The above reveals that increase in dissociation of hydrogen sulfide with increase in temperature in both cases (with and without xylene present) can be attributed to increased rate of thermal decomposition of hydrogen sulfide. Additionally, the increase in decomposition of hydrogen sulfide with xylene present can be attributed to increased chemical decomposition of hydrogen sulfide due to the abundance of hydrogen radicals released from dissociation of xylene at relatively lower temperatures.

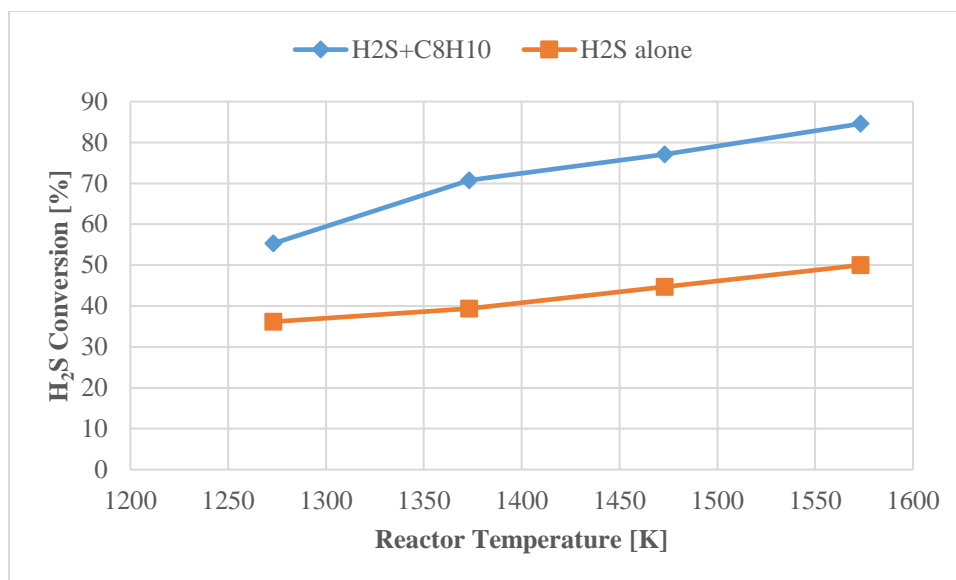


Figure 47. H₂S conversion as a function of temperature for 9.4% H₂S/0.6% C₈H₁₀ in 90% N₂ and 9.4% H₂S in 90.6% N₂ mixtures

4.2.5.3. Effect of C₈H₁₀ Amounts on H₂S Reformation

One of the problems associated with this method was carbon deposition. Since complete decomposition of xylene could be achieved at relatively low temperatures compared to those required for hydrogen sulfide decomposition due to the relatively higher endothermicity of H₂S thermal dissociation, xylene as well as all formed hydrocarbons continue to break down to carbon and hydrogen. The examined stoichiometric conditions assume complete conversion of the reactants to hydrogen and carbon disulfide. Since this assumption is not true, relative abundance of carbon compared to available sulfur species to form CS₂ results in carbon deposition. Carbon deposition was visually observed on inner surface of quartz reactor as well as outer and inner surfaces of the sampling probe at exit of the reactor. To estimate the relative rates of reaction to avoid carbon deposits under stoichiometric conditions, for 1 molecule of xylene, 16 molecules of hydrogen sulfide were required to decompose and provide

enough sulfur species to react with xylene and its derived species to form CS₂. To eliminate carbon deposition problem, two plausible routes can be taken. First one being to achieve decomposition of hydrogen sulfide at a rate that is ideally 16 times the rate of xylene decomposition. This route does not seem practical based on the results shown in the previous section. The other route is to decrease the amount of carbon introduced to the reaction pool to limit its relative abundance by reducing the composition of xylene in the inlet stream. The other way to view this is to provide more hydrogen sulfide that can decompose and provide sufficient sulfurous species to react with xylene and its derived species to form CS₂ rather than to deposit carbon on the surfaces. This route also emerges from the conclusion that thermal dissociation of H₂S is the rate limiting step of CS₂ formation that leads to carbon deposits. Therefore, relative abundance of H₂S should maneuver the reaction towards CS₂ formation rather than carbon deposition. CS₂ formation is expected to be limited due to the limited quantities of carbonaceous compounds introduced to the reaction. Following results are on the hydrogen produced, hydrogen sulfide destructed and carbon disulfide formed with inlet stream having H₂S/C₈H₁₀ mixture ratio of 16, 24 and 32, which represents 1, 1.5 and 2 times the stoichiometric ratio for this reaction. Figure 48 shows the amounts of hydrogen produced as well as remaining amounts of hydrogen sulfide at a temperature of 1473K and different H₂S/C₈H₁₀ ratios of 16, 24 and 32. The amounts of hydrogen was observed to decrease by 20% with increase in H₂S/C₈H₁₀ ratio from 16 to 32 due to decrease in the hydrogen constituent in the mixture. It can also be observed that the amounts of hydrogen sulfide in the products stream increased with increase in H₂S content in the inlet stream.

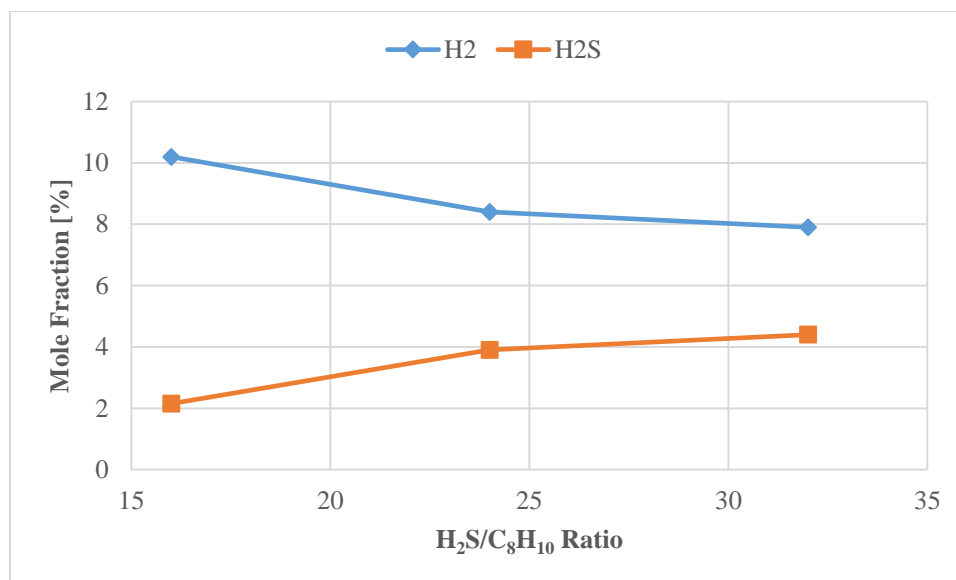


Figure 48. H₂ and H₂S with change in H₂S/C₈H₁₀ ratio (H₂S/C₈H₁₀ diluted in 90% N₂)

The increase in detected amounts of hydrogen sulfide with increase of H₂S/C₈H₁₀ ratio, shown in Figure 48, is attributed to lower conversion of hydrogen sulfide as shown in Figure 49. This is due to the limited role provided by extra H-radicals liberated from xylene. Therefore, decrease in the amounts of xylene in the inlet stream leads to decreased amounts of H-radical that enhances chemical decomposition of hydrogen sulfide. The decrease in inlet composition of xylene also leads to decrease in carbonaceous species that reacts to form CS₂.

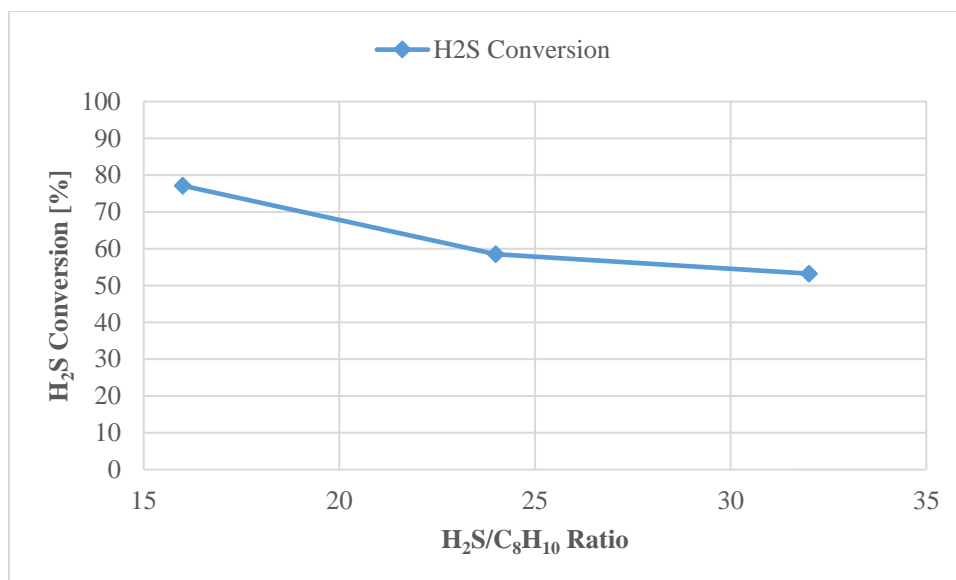


Figure 49. H₂S conversion as a function of H₂S/C₈H₁₀ ratio at temperature of 1473 K

Measured values on the formed CS₂ at different H₂S/C₈H₁₀ is shown in Figure 50. Formation of CS₂ decreased due to limited amounts of xylene introduced to the reaction pool, which limits the interaction between hydrocarbon radicals and sulfurous radical that results in formation of CS₂.

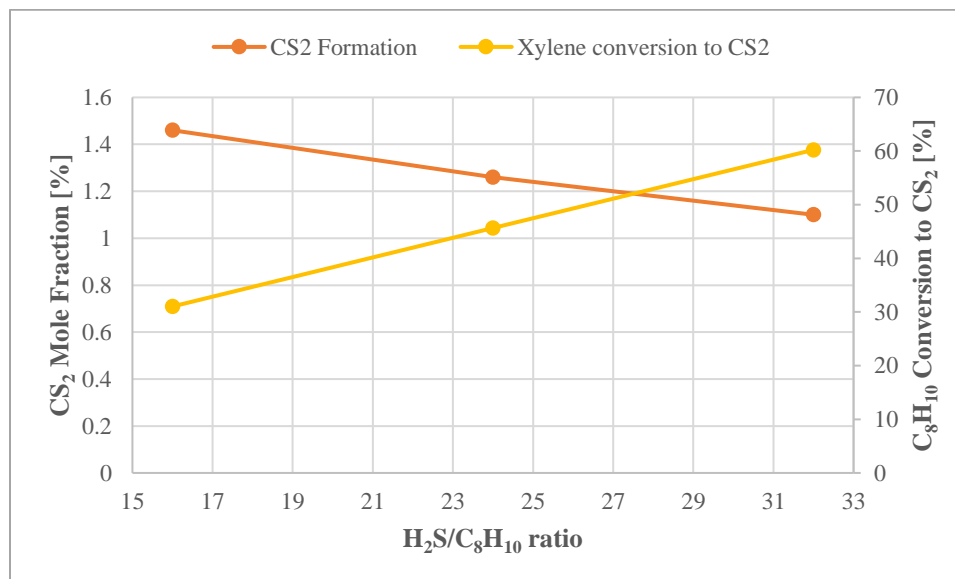


Figure 50. CS₂ mole fraction in the products stream and fraction of C₈H₁₀ converted to CS₂ as a function of H₂S/C₈H₁₀ ratio at temperature of 1473 K

The other undesired byproduct was the deposited carbon. Carbon deposition was visually observed at $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ ratio of 16. It was visually observed that carbon deposition decreased with increase in $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ ratio. However, based on measured values of CS_2 and given the composition of xylene in the inlet stream, element balance on carbon could be conducted assuming that carbon in xylene is either forming CS_2 or deposit on the inner surface of the reactor in the form carbon laydown. This assumption is reasonable, given that other carbonaceous compounds mainly in form of hydrocarbons were of the order of hundreds of ppms. This element balance assisted in determining the amount of xylene that formed CS_2 and the amount that dissociated to hydrogen and carbon. Increase in conversion of xylene to carbon disulfide with decrease of xylene composition in inlet stream, shown in Figure 50, depicts significant decrease in carbon deposition. However, since not all carbon in the xylene was converted to CS_2 even at the highest $\text{H}_2\text{S}/\text{C}_8\text{H}_{10}$ ratio, it suggests that carbon deposition was reduced but not completely eliminated. Although, carbon deposition was not visually apparent at later lengths of the reactor, this carbon deposition can be related to the earlier dissociation of xylene compared to hydrogen sulfide. This carbon laydown at early stages is attributed to the relatively lower thermal stability of xylene compared to hydrogen sulfide.

4.2.5.4. Summary

Experimental results presented here provide information on the reformation of hydrogen sulfide in the presence of xylene to produce hydrogen. The effect of xylene

addition to dissociation of hydrogen sulfide has been discussed and highlighted. The effect of reactor temperature on the amounts of hydrogen produced, carbon disulfide formed and hydrogen sulfide destructed has been investigated over a temperature range of 1273-1573 K at relatively long residence time. The results reveals positive effects of hydrogen sulfide destruction in the presence of xylene. Xylene enhanced the production of hydrogen and destruction of hydrogen sulfide but lead to the formation of carbon disulfide and carbon deposition on internal surfaces of the reactor. Increase in reactor temperature contributed to further enhance the effects achieved from xylene addition. The results showed improved reformation of hydrogen sulfide in the presence of xylene for treating hydrogen sulfide contaminated with hydrocarbon impurities. This new information provides plausible solutions to the problems affecting performance of Claus process reactors. The presence of hydrocarbon impurities enhanced the production of hydrogen and destruction of hydrogen sulfide via reformation unlike that seen in contemporary Claus reactors. Formation of CS₂ as by-product and deposition of carbon at low H₂S/C₈H₁₀ ratios can be overcome with no to minimal hindrance in the potential reformation of H₂S/C₈H₁₀ to hydrogen and sulfur.

4.2.6. Reformation of Hydrogen Sulfide in Presence of Toluene

Results on the reformation of H₂S in the presence of C₇H₈ were examined and are presented here in the following. The speciation of H₂ was quantified experimentally from simultaneous reformation of H₂S and C₇H₈ over a range of temperatures and different inlet compositions. The amounts of CS₂ formed was quantified under examined conditions as well as the occurrence of carbon deposition on reactor walls.

4.2.6.1. Effect of Reactor Temperature on Reformation of H₂S with C₇H₈

Present

Reformation of hydrogen sulfide in the presence of toluene was examined over range of temperatures of 1273-1573 K using a quartz tubular reactor at comparatively long residence time of 1 second. The effect of reactor temperature on the conversion of hydrogen sulfide and amounts of hydrogen produced was examined. The results were obtained from 9.33% H₂S / 0.67% C₇H₈ / 90% N₂ mixture, which reflects the H₂S/C₇H₈ stoichiometric ratio of 14 in reaction between hydrogen sulfide and toluene since N₂ was inert. Results on the amounts of hydrogen produced over the different temperatures examined are depicted in Figure 51. Hydrogen was observed to increase with increase in reactor temperature. Quantification of the remaining toluene in the products stream was not the focus of this study. However, an indication of presence of toluene or complete destruction of toluene could be obtained using FID detector within bounded detection limits. The results obtained showed absence of toluene at temperatures higher than 1373 K. This reveals that toluene has less thermal stability compared to hydrogen sulfide. Consequently, thermal decomposition of toluene initiated thermally via unimolecular dissociation reaction at first and continued to decompose thermally in the same time it decomposes chemically via bimolecular reaction with the active radicals such as H radical as well as other hydrocarbon radicals. Further dissociation of toluene as well as formed hydrocarbons to carbon and gases was the most favorable route at this range of temperatures with most of the gases being hydrogen except few others with concentration in hundreds of ppm's.

Since a mixture of hydrogen sulfide and toluene has higher hydrogen feedstock, presence of toluene was expected to increase the amounts of hydrogen produced. To quantify the upsurge in hydrogen production, a comparison between amounts of hydrogen produced with and without toluene present in the reactant stream was made. In both cases, the composition of hydrogen sulfide remained the same to eliminate the effect of difference in amounts of H_2S concentration. The comparison between the amounts of hydrogen produced is depicted in Figure 51. Enhanced hydrogen production with toluene present can be observed even at the lowest temperature examined. The complete conversion of toluene was identified from the absence of any hydrocarbon detected by the FID at any temperature other than 1273 K.

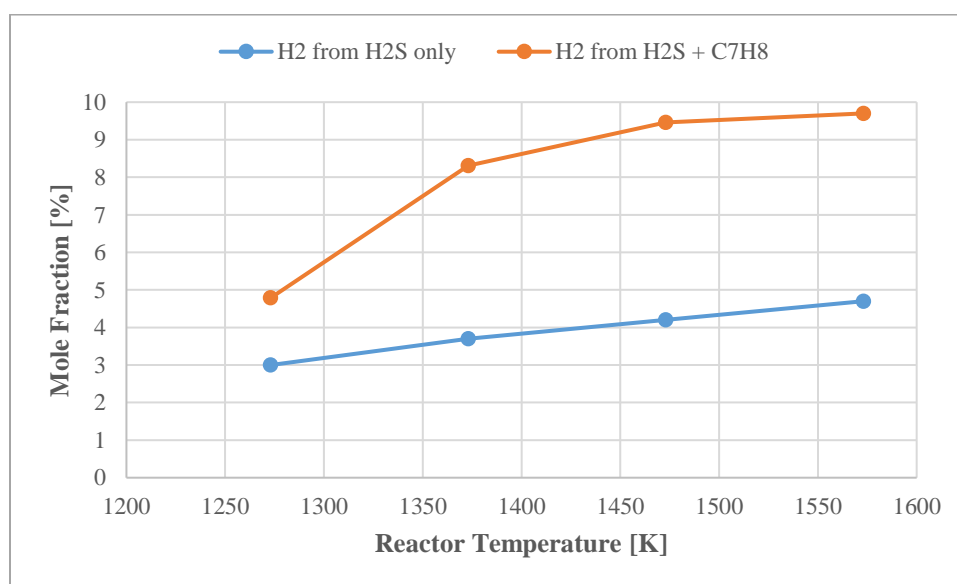


Figure 51. H_2 produced from H_2S with C_7H_8 and H_2S only at different temperatures

To evaluate this further, the effect of presence of toluene on hydrogen sulfide destruction must be isolated and quantified regardless of the increased hydrogen production. The comparison reveals one of three possibilities. First being that the

increase in hydrogen production is due to the increased hydrogen in feedstock. However, the toluene hindered hydrogen sulfide conversion. Second being that enhanced hydrogen production achieved in the presence of toluene was due to simultaneous decomposition of hydrogen sulfide and toluene while presence of toluene did not affect hydrogen sulfide conversion. Last one being that hydrogen production increased due to increased hydrogen feedstock in the $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ mixture as well as increased hydrogen sulfide conversion. Figure 52 provides a comparison on the conversion of hydrogen sulfide in both cases given earlier and depicts that the last possibility is valid. The presence of toluene not only increased hydrogen feedstock in the inlet stream but also fostered destruction of hydrogen sulfide which reveals enhanced potential of this method as a treatment method of hydrogen sulfide stream. The increased conversion of hydrogen sulfide can be viewed from two different perspectives of thermodynamic and kinetic. Thermal dissociation of hydrogens sulfide is known to suffer from the chemical equilibrium limitation due to backward reactions between hydrogen and sulfur to form hydrogen sulfide. However, in presence of toluene, one of the main products of hydrogen sulfide dissociation is devoted for the inevitable formation of carbon disulfide. This consumption of sulfur relocates the equilibrium limit forward for higher hydrogens sulfide conversion to amend for sulfur consumption. This supports enhanced destruction of hydrogen sulfide in the presence of toluene to be thermodynamically favored.

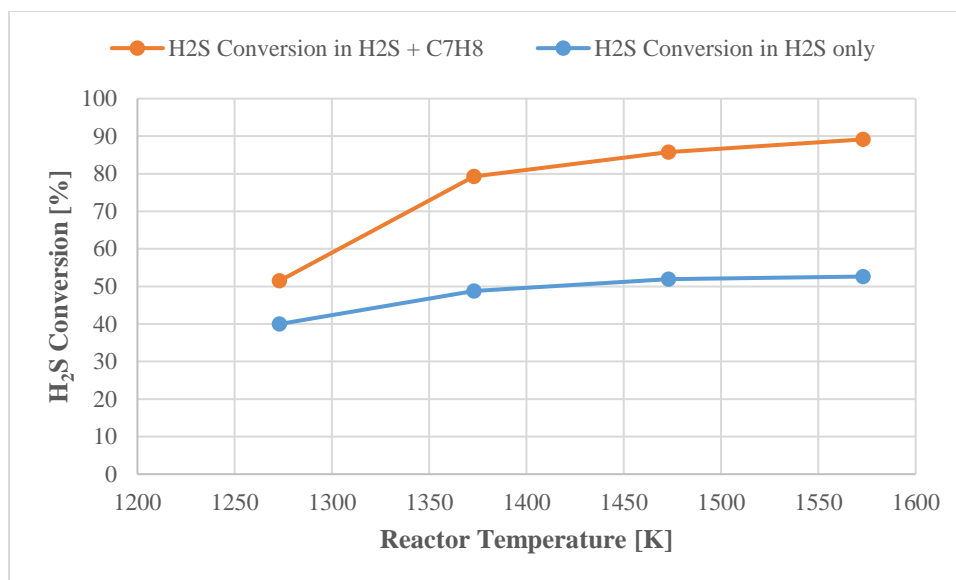


Figure 52. H₂S conversion as a function of temperature for 9.33% H₂S/0.67% C₇H₈ in 90% N₂ and 9.33% H₂S in 90.67% N₂ mixtures

The presence of hydrocarbon-toluene in the thermal dissociation of hydrogen sulfide provided interaction between hydrocarbon and sulfurous radicals at very high probability as well as to promote the formation of carbonaceous-sulfurous compounds, carbon disulfide in this case. Under the examined conditions, carbon disulfide was not the only carbon-constituted compound formed; the carbon itself deposited on the inner surface of the reactor. Given the complete conversion of toluene at temperatures higher than 1373 and the observed carbon deposit at all temperatures, one can infer that the formation of carbon disulfide is limited by hydrogen sulfide thermal decomposition which supports the findings of Chin et al. [112] and Karan and Behie [79].

Composition of carbon disulfide evolved from the stoichiometric H₂S/C₇H₈ mixture at different temperatures ranging from 1273-1573 K and at residence time of 1 sec is shown in Figure 53. Carbon disulfide was observed to increase with increase in temperature. Since formation of carbon disulfide is limited by thermal dissociation

of hydrogen sulfide, increased hydrogen sulfide dissociation at high temperatures provided sulfurous species to the reaction pool to further promote the formation of carbon disulfide. This resulted in increased carbon disulfide composition in products stream with increase in temperature.

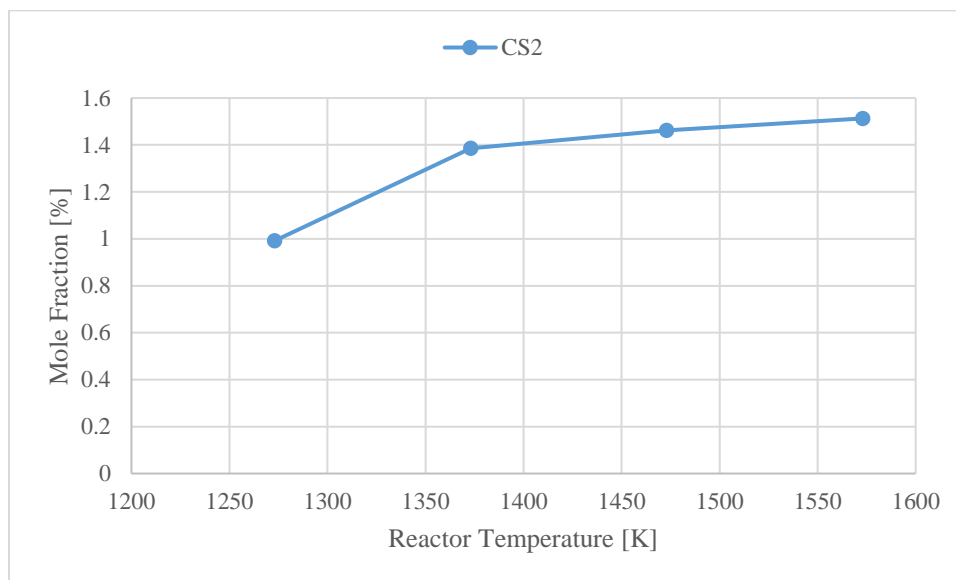


Figure 53. CS₂ formed from reaction between H₂S and C₇H₈ at temperature range of 1273-1573K

4.2.6.2. Effect of C₇H₈ Composition on H₂S Reformation

At the stoichiometric ratio of H₂S/C₇H₈ which corresponds to the inlet stream composition of 9.33% H₂S / 0.67% C₇H₈ / 90% N₂, carbon deposits could visually be observed on the inner surface of the reactor at all the temperatures examined. Due to the comparatively lower thermal stability of toluene which lead to complete decomposition at temperatures lower than those required for complete conversion of hydrogen sulfide, the main products of toluene dissociation were carbon, hydrogen and hydrocarbon radicals. However, at the same temperature, incomplete dissociation of hydrogen sulfide makes the reaction pool to lack sulfur and sulfurous radicals for

reaction with the products from toluene dissociation. This relative scarcity of sulfur to form carbon disulfide blocks routes for carbon consumption other than forming solid carbon deposits. The problem associated with carbon deposits tends to appear while accelerating the dissociation reaction using catalysts. This carbon deposits can poison the catalyst by significantly reducing the active surface area. In order to eliminate carbon deposits in the reactor, two intuitive routes can be taken. First route is to achieve higher hydrogen sulfide dissociation rate to produce enough sulfur and sulfurous radicals to react with formed carbon and hydrocarbon radicals and form carbon disulfide. To estimate the relative rate at which hydrogen disulfide gets dissociated, formation of carbon disulfide molecule will require 14 molecules of hydrogen sulfide and 1 molecule of toluene for stoichiometric conditions. Given this stoichiometry, decomposing hydrogen sulfide at a rate 14 times faster than toluene is impractical with the equilibrium limitations and high endothermicity of hydrogen sulfide compared to toluene. However, due to the enhanced destruction of hydrogen sulfide in the presence of toluene, the factor of relative rates of decomposition of 14 may be excessive. The other route of eliminating carbon deposits on the reactor is to reduce the amounts of carbon content introduced to the reaction pool by increasing $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio, which excludes the redundant carbon that leads to carbon deposits other than to react and form carbon disulfide. Consequently, different $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratios were examined in the same reactor at the same residence time of 1 second at constant temperature of 1473 K for all the $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratios. $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio of 14 that reflects stoichiometry also represented the baseline case for this comparison. Other ratios of 21 and 28 were examined that represents 1.5 and 2 times the stoichiometry ratio values. This mixture

was kept 10% in all cases with the remaining being nitrogen. The objective here was to eliminate carbon deposits and quantify the reduction in carbon disulfide formation from reduction in toluene composition. Also, the impact of reducing composition of toluene in the mixture was explored to determine the amounts of hydrogen produced and hydrogen sulfide destructed. The results on the hydrogen produced from different mixtures ratios as well as remaining undecomposed hydrogen sulfide are shown in Figure 54. Amounts of hydrogen produced were observed to decrease with increase in $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio. This decrease pertains to reduced hydrogen constituent from the decrease in toluene composition in the mixture. However, it can also be related to lower conversion of hydrogen sulfide. Figure 54 also shows increased amounts of hydrogen sulfide remaining in the products stream, which can be from two reasons of increased hydrogen sulfide concentration in the inlet stream or lower conversion of hydrogen sulfide due to lower composition of toluene in the mixture. However, from the given inlet composition in the respective cases and increased hydrogen sulfide amounts remaining in the products stream, it can be conjectured that the conversion of hydrogen sulfide was reduced.

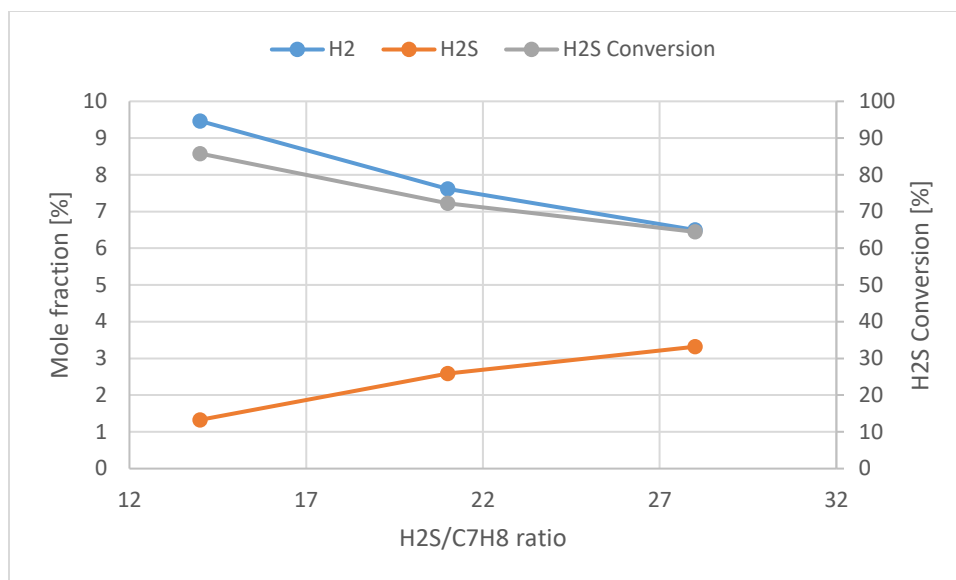


Figure 54. H₂ and H₂S with change in H₂S/C₇H₈ ratio (H₂S/C₇H₈ diluted in 90% N₂)

The results on the decreased conversion of hydrogen sulfide due to decrease in toluene amounts in the inlet stream is shown in Figure 54. Since the decrease in the conversion of hydrogen sulfide is strongly related to the less amounts of toluene present in the mixture, this can be attributed to the comparatively lower amounts of H radical introduced to the reaction pool by toluene decomposition. The reduced amounts of H-radical in the reaction pool impacts the chemical decomposition of hydrogen sulfide to cause an increase in hydrogen sulfide amounts in the products stream. Also, less toluene in the inlet stream limits the carbon constituent required for CS₂ formation. Although, formation of CS₂ is undesirable, it consumes sulfur and shifts equilibrium towards more consumption of hydrogen sulfide. Lower carbon constituent reduces consumption of sulfur to form CS₂, which get the equilibrium limit back again closer to the equilibrium limit of thermal dissociation of hydrogen sulfide alone.

Measured values on the formed CS₂ at different H₂S/C₇H₈ are shown in Figure 55. Formation of CS₂ decreased due to limited amounts of toluene introduced to the

reaction pool, which limits the interaction between hydrocarbon radicals and sulfurous radical that results in formation of CS_2 . The other undesired byproduct was the deposited carbon. Carbon deposition was visually observed at $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio of 14. It was visually observed that carbon deposition decreased with increase in $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio. However, based on measured values of CS_2 and given the composition of toluene in the inlet stream, element balance on carbon could be conducted assuming that carbon in toluene is either forming CS_2 or deposit on the inner surface of the reactor in the form carbon laydown. This assumption is reasonable, given that other carbonaceous compounds mainly in form of hydrocarbons were of the order of hundreds of ppms. This element balance assisted in determining the amount of toluene that formed CS_2 and the amount that dissociated to hydrogen and carbon. Increase in conversion of toluene to carbon disulfide with decrease of toluene composition in inlet stream, shown in Figure 55, depicts significant decrease in carbon deposition. However, since not all carbon in the toluene was converted to CS_2 even at the highest $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ ratio, it suggests that carbon deposition was reduced but not completely eliminated. Although, carbon deposition was not visually apparent at later lengths of the reactor, this carbon deposition can be related to the earlier dissociation of toluene compared to hydrogen sulfide. This carbon laydown at early stages is attributed to the relatively lower thermal stability of toluene compared to hydrogen sulfide.

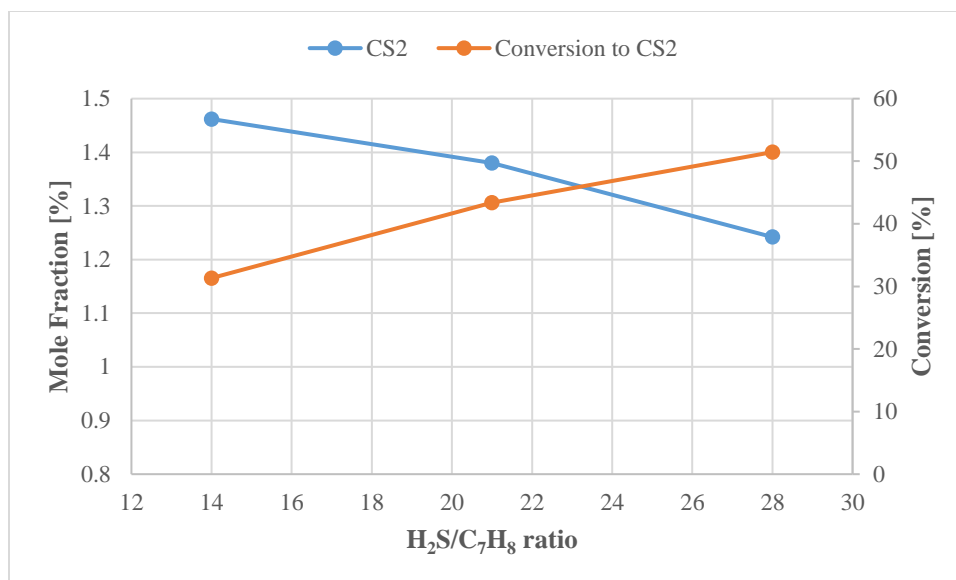


Figure 55. CS₂ mole fraction in the products stream and fraction of C₇H₈ converted to CS₂ as a function of H₂S/C₇H₈ ratio at temperature of 1473 K

4.2.6.3. Summary

Experimental data on hydrogen production via thermal reformation of hydrogen sulfide in presence of toluene have been reported here. Effect of reactor temperature in range of 1273-1573K as well as H₂S/C₇H₈ ratio in inlet stream at relatively long residence time was examined. These operational parameters were found to directly affect the amounts of hydrogen produced, hydrogen sulfide destructed and carbon disulfide formed. The role played by presence of toluene was established by comparing the amounts of hydrogen produced from hydrogen sulfide with or without the presence of toluene in the H₂S. Another comparison was also made between hydrogen sulfide destruction in both cases of without and with toluene. The results revealed enhanced destruction of hydrogen sulfide as well as more hydrogen production from hydrogen sulfide in case of presence of toluene. The results showed significant effect of reactor temperature along with increased production of hydrogen and hydrogen sulfide

conversion at increased reactor temperatures. At higher reactor temperatures, the formation of carbon disulfide increased. $\text{H}_2\text{S}/\text{C}_7\text{H}_8$ mixture composition was an important parameter that affects the amounts of carbon disulfide formed as well as the carbon deposition on reactor surface. The results showed that presence of toluene is beneficial for thermal reformation of hydrogen sulfide as an innovative treatment technology of hydrogen sulfide stream with no adverse impact on treatment process on its performance, unlike that observed in Claus reactors.

Chapter 5: Conclusions and Research Contributions

Research presented in this dissertation revealed several facts about the chemical kinetics of H_2S thermal decomposition, conditions under which other sulfurous compounds are formed, and effect of reactor conditions on H_2S pyrolysis and evaluate the thermal decomposition of hydrogen sulfide stream as an alternative method to treat hydrogen sulfide. In this chapter, we discuss the main conclusions drawn out of this research and the research major contributions.

5.1. Conclusions

The work presented here started with studying the effect of reactor parameters on the pyrolysis of hydrogen sulfide only. Then a numerical investigation for H_2S pyrolysis was developed aiming to identify the most dominant chemical kinetic pathways. At this stage the high endothermicity as well as the equilibrium limitation has been proven experimentally. Consequently, the research has been directed towards alleviating these two obstacles. Therefore, partial oxidation of hydrogen sulfide under rich conditions has been studied as a method to mitigate the high-energy input requirement. On the other hand, pyrolysis of hydrogen sulfide in presence of some impurities that are naturally accompanying hydrogen sulfide stream in practice. Most of the impurities examined in this research are hydrogen constituted; hence, they were expected to enhance production of hydrogen from hydrogen sulfide. The effect of presence of each impurity is demonstrated separately. Issues arising from presence of these impurities in the inlet stream has also been addressed.

5.2. Production of Hydrogen via Hydrogen Sulfide Pyrolysis and Partial Oxidation

Effect of reactor parameters on hydrogen sulfide pyrolysis including temperature and partial pressure has been investigated experimentally and numerically. The reaction is highly endothermic and is favored at high temperature. A high reactor temperature significantly reduces the reactor residence time required for high conversion of hydrogen sulfide. A residence time of 1.2 second was long enough to reach an asymptotic steady state value at all temperatures above 1273 K. Increase in the inlet concentration of hydrogen sulfide hindered hydrogen production and hydrogen sulfide conversion.

A detailed reaction mechanism has been modified to simulate the thermal dissociation of hydrogen sulfide. Experimental results obtained at temperatures up to 1473 K using a plug flow tubular reactor were used to validate the model simulations. The qualitative agreement between the experimental results and simulations provided the identification of the various reaction pathways as well as the most dominant reactions. The role of different radicals H, S, SH and HS₂ has been highlighted in decomposition/recombination reactions. SH radical plays an important role in the recombination reaction to form H₂S again.

Hydrogen production via partial oxidation of hydrogen sulfide has shown potential to alleviate the thermal load required for hydrogen sulfide dissociation. A comparison between amounts of hydrogen produced both without and with oxygen injection revealed decreased production of hydrogen with oxygen present but higher hydrogen sulfide conversion over temperature range of 1273-1473 K. The decrease in production of hydrogen was lower in presence of oxygen due to partial consumption of

hydrogen formed to H_2O . The absence of SO_2 with oxygen present in the hydrogen sulfide stream was featured at all the temperature investigated.

5.3. Syngas Recovery from Acid Gas

Pyrolysis of acid gas was examined over a 1250–1475 K temperature range at relatively high residence time. This pyrolysis resulted in conversion to syngas while also recovering sulfur. It has been found that reactor temperature and acid gas composition are the main parameters affecting the conversion of H_2S and CO_2 (acid gas) to produce syngas with a wide range of H_2 to CO ratio. Destruction of H_2S increased in presence of CO_2 as well as production of CO while there was reduction in H_2 produced. Lean acid gas with H_2S content of lower than 60% and high CO_2 content - which may impose operational difficulties with the processing of lean acid gas in Claus process - offers potential for syngas production that is suitable for both gas engine application and ammonia production. The presence of impurities, such as hydrocarbons is expected to further enhance the production of hydrogen-rich syngas.

5.4. Enhanced Hydrogen Production in Presence of Different Hydrocarbon Impurities

Production of hydrogen from hydrogen sulfide contaminated with hydrocarbons that naturally exist in separated-out hydrogen sulfide stream has been examined. Hydrocarbons of interest are methane, benzene, toluene and xylene commonly called BTX. Traditionally, investigations on hydrocarbons starts with methane. Examination of reformation of hydrogen sulfide in presence of methane were conducted over temperature range of 1273 – 1673 K at relatively long residence time of 1.2 sec.. The presence of methane was proven to foster production of hydrogen from

hydrogen sulfide. It also enhanced destruction of hydrogen sulfide over the entire range of investigated temperatures. The production of hydrogen and destruction of hydrogen sulfide was increasing with temperature. On the other hand, presence of methane promoted formation of CS_2 . Also, carbon deposition was visually observed over the whole range of temperature. The other parameter that was studied was the inlet composition and it was found that carbon deposition can be decreased significantly by increasing $\text{H}_2\text{S}/\text{CH}_4$ ratio higher than stoichiometric ratio of 2. This also limits the formation of CS_2 . Since the methane content in the stream decreased, the amounts of hydrogen produced were decreased. Also, the role played by presence of methane via chemical decomposition of hydrogen sulfide was reduced.

Further investigation on thermal decomposition of $\text{H}_2\text{S}/\text{CH}_4$ mixture has been done using experimental data over the same range of temperatures studied before but at different residence time. A reaction mechanism has been developed and validated against the obtained experimental data. It was able to predict the amounts of hydrogen produced and the conversion of both methane and hydrogen sulfide with less than 15% error. The numerical simulations highlighted the most dominant reaction pathways

Chemical decomposition of hydrogen sulfide via reaction with radicals was dominating the destruction of hydrogen sulfide. As much as 95% hydrogen recovery has been demonstrated experimentally from a mixture of hydrogen sulfide and methane. Increase in temperature to 1373 K shortened dramatically the residence time required to reach the asymptotic steady state composition along with significantly increased amounts of hydrogen (double amounts of hydrogen was achieved in presence

of methane at temperatures higher than 1373K) as compared to that obtained from H₂S alone.

This was followed by experimental examination of hydrogen production via thermal reformation of hydrogen sulfide in presence of benzene and xylene as common contaminants. Effect of each contaminant was studied separately over temperature range of 1273-1573K and at residence time of 1.2 seconds. First, the reaction between H₂S and C₆H₆ or C₈H₁₀ was studied under stoichiometric conditions. Then higher H₂S/C₆H₆ or H₂S/C₈H₁₀ ratios were examined. Similar to methane, benzene and xylene were found to enhance H₂ production, H₂S destruction but also promote formation of CS₂ and deposition of carbon. Based on the understanding of reaction between hydrogen sulfide and methane, the role played by benzene and xylene was also related to equilibrium shift due to formation of CS₂ and enhanced chemical decomposition of H₂S. Results obtained from thermal decomposition of hydrogen sulfide with hydrocarbon were comparable in terms of H₂S conversion. Noting that the stoichiometry in all experiments of H₂S in presence of hydrocarbon guaranteed same sulfur to carbon ratio. However, amounts of hydrogen provided by each hydrocarbon differs. This suggests that presence of carbon and formation of CS₂ are the main cause of increased H₂S conversion compared to role provided by increased hydrogen radicals.

5.5. Research Contributions

Research presented in this dissertation resulted in several contributions in the area of H₂S thermal decomposition for enhanced hydrogen production:

- Demonstrated the potential of hydrogen production via partial oxidation of hydrogen sulfide under fuel rich conditions ($\phi = 6 - 13.5$).

- Identified reactor conditions that mitigate formation of unwanted sulfur dioxide in the presence of trace amounts of O₂ (Temperature > 1273K, $\phi > 6$).
- Determine the effect of contaminants (including CO₂, CH₄, C₆H₆, and C₈H₁₀) in acid gas on the pyrolysis process over temperature range of 1273-1573K.
- Defined the region of optimum operating conditions with respect to acid gas composition for enhanced hydrogen production from destruction of H₂S.
(Temperature > 1373K, $\left[\frac{H_2S}{HC}\right] > 2 \times \left[\frac{H_2S}{HC}\right]_{stoichiometric}$)
- Quantified the amounts of other stable sulfurous byproducts formed during pyrolysis of contaminated hydrogen sulfide stream with hydrocarbons.
- Validated chemical reaction mechanism for hydrogen sulfide pyrolysis and a mixture of hydrogen sulfide with methane.
- Identified the most dominant chemical kinetic pathways in hydrogen sulfide alone and mixture of hydrogen sulfide and methane pyrolysis.

Chapter 6: Recommendations for Future Work

The research presented in this dissertation focused on production of hydrogen from hydrogen sulfide under different conditions. Identification of dominant reaction pathways and demonstration of effect of different reactor parameters was provided experimentally and numerically. Nevertheless, this work can be extended to new horizons that have been opened through this research.

6.1. Production of Hydrogen from Hydrogen Sulfide in Presence of Ammonia

In continuation of production of hydrogen from hydrogen sulfide with impurities present, ammonia is one of the hydrogen-constituted impurities that is expected to enhance production of hydrogen. Thus, enhanced production of the clean, green and zero-emission hydrogen fuel from thermal decomposition of contaminated hydrogen sulfide stream with ammonia is to be focused on. Since ammonia is hydrogen constituted without carbon and other impurities has hydrogen and carbon, so the role of hydrogen radicals and the role of carbon in these hydrocarbons-investigated in this research-can be distinguished.

6.2.Detailed Radical Reaction Mechanism for Pyrolysis of Hydrogen Sulfide Stream

Thermal decomposition of hydrogen sulfide only has been studied experimentally and numerically. The numerical simulations have been validated against experimental results. However, most of these studies are based on measurements of stable species. In addition, these studies focused on thermal

decomposition of hydrogen sulfide only. Presence of contaminants were proven to affect the thermal dissociation reaction significantly. Since these contaminants supply/consume radicals and have this impact on the reaction pool, quantifications of radicals in the reaction pool under different conditions is of pinnacle importance on the understanding of reaction of hydrogen sulfide with different species. The species of interest are those naturally accompanying hydrogen sulfide which include: carbon dioxide, methane, ammonia, benzene, toluene and xylene. This investigation will not only benefit the area of production of hydrogen from hydrogen sulfide but its benefits also extends to identifying the reaction pathways between different species in currently employed Claus reactor.

6.3. Production of Hydrogen from Hydrogen Sulfide Filtration

Combustion

Production of hydrogen via thermal dissociation of hydrogen sulfide is known to be highly endothermic. This high energy input requirement is an obstacle hindering advance in application of this technology. However, production of hydrogen via partial oxidation of hydrogen sulfide without formation of any sulfur oxides in the final stream has been proven experimentally. Filtration combustion which involves exothermic reaction within a porous matrix offers heat recirculation from the hot products to the incoming reactants. This heat recirculation expands the flammability limits to allow for richer mixtures to be burnt. This investigation represents a good step towards making production of hydrogen from hydrogen sulfide an autothermal process.

6.4. Production of Syngas from Acid Gas

Alternative utilization and more efficient treatment of acid gas are also required to preserve our environment from sulfur-bearing fuels while simultaneously enhancing energy generation. This study has shown that both syngas and sulfur can be produced from acid gas under certain reactor operational conditions. This is an attractive alternative since the large volume of CO₂ in acid gas can be captured from the produced syngas. Moreover, sulfur recovery from lean acid gas that contains higher CO₂ content than H₂S as well as hydrocarbon impurities in a Claus process pose severe technical and environmental issues. The H₂ and CO produced (syngas) can then be used in industry for energy and power applications. This can be achieved with minimal adverse effect to the environment, human health and building aesthetics. Syngas can be used as a fuel for gas engines, or to produce valuable chemicals, such as ammonia.

References

- [1] P. J. Crutzen, "The possible importance of CSO for the sulfate layer of the stratosphere," *Geophysical Research Letters*, vol. 3, pp. 73-76, 1976.
- [2] G. S. Tyndall and A. R. Ravishankara, "Atmospheric oxidation of reduced sulfur species," *International Journal of Chemical Kinetics*, vol. 23, pp. 483-527, 1991.
- [3] R. P. Wayne, *Chemistry of Atmospheres: An Introduction to the Chemistry of the Atmospheres of Earth, the Planets, and their Satellites*, Oxford University Press, 1985.
- [4] "U.S. Department of Labor, Occupational Safety & Health Administration," [Online]. Available: <https://www.osha.gov/SLTC/hydrogensulfide/hazards.html>.
- [5] "Chevron Philips Chemical Company," [Online]. Available: http://www.cpchem.com/msds/100000067417_SDS_US_EN.PDF.
- [6] V. Chandra Srivastava, "An evaluation of desulfurization technologies for sulfur removal from liquid fuels," *RSC Adv.*, vol. 2, no. 3, pp. 759-783, 2012.
- [7] D. Wall, "A Higher Tier," *Hydrocarbon Engineering*, September 2013.
- [8] P. N. James, *Developing Clean Fuels: Novel Techniques for Desulfurization*, vol. Ph.D. Dissertation, Princeton University, 2006.
- [9] G. T. Austin, *Shreve's Chemical Process Industries: Fifth Edition*, McGraw-Hill Book Company, 1984.
- [10] S. E. Bonde, W. Gore, G. E. Dolbear and E. R. Skov, "Selective Oxidation and Extraction of Sulfur-Containing Compounds to Economically Achieve Ultra-Low Diesel Fuel Sulfur Requirements," in *American Chemical Society, Division of Petroleum Chemistry*, 2000.
- [11] C. Song, "An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel," *Catalysis Today*, vol. 86, pp. 211-263, 2003.
- [12] R. El-Bishtawi and N. Haimour, "Claus recycle with double combustion process," *Fuel Processing Technology*, vol. 86, pp. 245-260, 2004.
- [13] A. B. Jensen and C. Webb, "Treatment of H₂S-containing gases: A review of microbiological alternatives," *Enzyme and Microbial Technology*, vol. 17, pp. 2-10, 1995.
- [14] "NaturalGas.org," NGSA, [Online]. Available: <http://naturalgas.org/naturalgas/processing-ng/>.
- [15] A. L. Kohl and R. B. Nielsen, "Chapter 2 - Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal," in *Gas Purification*, Fifth Edition ed., Houston, Texas: Gulf Professional Publishing, 1997, pp. 40 - 186.

- [16] R. Larraz, "Influence of fractal pore structure in Claus catalyst performance," *Chemical Engineering Journal* , vol. 86, pp. 309-317, 2002.
- [17] A. E. Cover, D. A. Hubbard, S. K. Jain, K. V. Shah, P. B. Koneru and E. W. Wong, "Review of Selected Sulfur Recovery Processes for SNG Production," Gas Research Institute, Houston, Texas, 1985.
- [18] M. Sassi and A. K. Gupta, "Sulfur Recovery from Acid Gas Using the Claus Process and High Temperature Air Combustion (HiTAC) Technology," *American Journal of Environmental Sciences*, vol. 4, no. 5, pp. 502-511, 2008.
- [19] H. Selim, A. K. Gupta and M. Sassi, "Novel error propagation approach for reducing H₂S/O₂ reaction mechanism," *Applied Energy* , vol. 93, pp. 116-124, 2012.
- [20] J. Zaman and A. Chakma, "Production of hydrogen and sulfur from hydrogen sulfide," *Fuel Processing Technology*, vol. 41, pp. 159-198, 1995.
- [21] D. W. Kalina and E. T. M. Jr., "Indirect hydrogen sulfide conversion—I. An acidic electrochemical process," *International Journal of Hydrogen Energy* , vol. 10, pp. 157-162, 1985.
- [22] D. W. Kalina and E. T. M. Jr., "Indirect hydrogen sulfide conversion—II. A basic electrochemical process," *International Journal of Hydrogen Energy* , vol. 10, pp. 163-167, 1985.
- [23] R. C. Kainthla and J. O. Bockris, "Photoelectrolysis of H₂S using an n-CdSe photoanode," *International Journal of Hydrogen Energy*, vol. 12, pp. 23-26, 1987.
- [24] N. Serpone, E. Borgarello and M. Gratzel, "Visible light induced generation of hydrogen from H₂S in mixed semiconductor dispersions; improved efficiency through inter-particle electron transfer," *J. Chem. Soc., Chem. Commun.*, no. 6, pp. 342-344, 1984.
- [25] L. R. Grzyll, J. J. Thomas and R. G. Barile, "Photoelectrochemical conversion of hydrogen sulfide to hydrogen using artificial light and solar radiation," *International Journal of Hydrogen Energy*, vol. 14, pp. 647-651, 1989.
- [26] S. A. Naman, S. M. Aliwi and K. Al-Emara, "Hydrogen production from the splitting of H₂S by visible light irradiation of vanadium sulfides dispersion loaded with RuO₂," *International Journal of Hydrogen Energy*, vol. 11, pp. 33-38, 1986.
- [27] L. Zhao, Y. Wang, X. Li, A. Wang, C. Song and Y. Hu, "Hydrogen production via decomposition of hydrogen sulfide by synergy of non-thermal plasma and semiconductor catalysis," *International Journal of Hydrogen Energy* , vol. 38, pp. 14415-14423, 2013.
- [28] E. L. Reddy, V. M. Biju and C. Subrahmanyam, "Hydrogen production from hydrogen sulfide in a packed-bed DBD reactor," *International Journal of Hydrogen Energy*, vol. 37, pp. 8217-8222, 2012.
- [29] K. Gutsol, R. Robinson, A. Rabinovich, A. Gutsol and A. Fridman, "High conversion of hydrogen sulfide in gliding arc plasmatron," *International Journal of Hydrogen Energy* , vol. 42, pp. 68-75, 2017.

- [30] X. Dang, J. Huang, L. Kang, T. Wu and Q. Zhang, "Research on Decomposition of Hydrogen Sulfide Using Nonthermal Plasma with Metal Oxide Catalysis," *Energy Procedia*, vol. 16, pp. 856-862, 2012.
- [31] K. Gutsol, T. Nunnally, A. Rabinovich, A. Fridman, A. Starikovskiy, A. Gutsol and A. Kemoun, "Plasma assisted dissociation of hydrogen sulfide," *International Journal of Hydrogen Energy*, vol. 37, pp. 1335-1347, 2012.
- [32] R. L. Mora, "Sulphur condensation influence in Claus catalyst performance," *Journal of Hazardous Materials*, vol. 79, pp. 103-115, 2000.
- [33] C. H. Muller, K. Schofield, M. Steinberg and H. P. Broida, "Sulfur chemistry in flames," *Symposium (International) on Combustion*, vol. 17, pp. 867-879, 1979.
- [34] A. Levy, E. L. Merryman and W. T. Reid, "Mechanisms of formation of sulfur oxides in combustion," *Environmental Science & Technology*, vol. 4, pp. 653-662, 1970.
- [35] A. J. Hynes and P. H. Wine, "Kinetics and Mechanisms of the Oxidation of Gaseous Sulfur Compounds," in *Gas-Phase Combustion Chemistry*, W. C. Gardiner, Ed., New, York: Springer New York, 2000, pp. 343-388.
- [36] K. Tsuchiya, K. Kamiya and H. Matsui, "Studies on the oxidation mechanism of H₂S based on direct examination of the key reactions," *International Journal of Chemical Kinetics*, vol. 29, pp. 57-66, 1997.
- [37] C. F. Cullis and M. F. R. Mulcahy, "The kinetics of combustion of gaseous sulphur compounds," *Combustion and Flame*, vol. 18, pp. 225-292, 1972.
- [38] K. Schofield, "The kinetic nature of sulfur's chemistry in flames," *Combustion and Flame*, vol. 124, pp. 137-155, 2001.
- [39] F. G. Cerru, A. Kronenburg and R. P. Lindstedt, "Systematically reduced chemical mechanisms for sulfur oxidation and pyrolysis," *Combustion and Flame*, vol. 146, pp. 437-455, 2006.
- [40] G. W. Jones, W. P. Yant and L. B. Berger, "The Explosibility of Hydrogen Sulfide in Air," *Industrial & Engineering Chemistry*, vol. 16, pp. 353-355, 1924.
- [41] J. N. Bradley and D. C. Dobson, "Oxidation of Hydrogen Sulfide in Shock Waves. I. Absorption Studies of OH and SO₂ in H₂S–O₂–Ar Mixtures," *The Journal of Chemical Physics*, vol. 46, p. 2865, 1967.
- [42] H. A. Bennett and A. Meisen, "Experimental determination of air-h₂s equilibria under claus furnace conditions," *The Canadian Journal of Chemical Engineering*, vol. 59, pp. 532-539, 1981.
- [43] D. S. Chamberlin and D. R. Clarke, "Flame Speed of Hydrogen Sulfide," *Industrial & Engineering Chemistry*, vol. 20, pp. 1016-1018, 1928.
- [44] M. E. D. Raymont, "Role of hydrogen in Claus plants," *Hydrocarbon Process.; (United States)*, vol. 54:5, May 1975.
- [45] P. D. Clark, N. I. Dowling, M. Huang, W. Y. Svrcek and W. D. Monnery, "Mechanisms of CO and COS Formation in the Claus Furnace," *Industrial & Engineering Chemistry Research*, vol. 40, pp. 497-508, 2001.

- [46] K. A. Hawboldt, W. D. Monnery and W. Y. Svrcek, "New experimental data and kinetic rate expression for H₂S pyrolysis and re-association," *Chemical Engineering Science*, vol. 55, pp. 957-966, 2000.
- [47] V. Kaloidas and N. Papayannakos, "Kinetics of thermal, non-catalytic decomposition of hydrogen sulphide," *Chemical Engineering Science*, vol. 44, pp. 2493-2500, 1989.
- [48] A. A. Adesina, V. Meeyoo and G. Foulds, "Thermolysis of hydrogen sulphide in an open tubular reactor," *International Journal of Hydrogen Energy*, vol. 20, pp. 777-783, 1995.
- [49] W. S. Harvey, J. H. Davidson and E. A. Fletcher, "Thermolysis of Hydrogen Sulfide in the Temperature Range 1350–1600 K," *Industrial & Engineering Chemistry Research*, vol. 37, pp. 2323-2332, 1998.
- [50] N. I. Dowling, J. B. Hyne and D. M. Brown, "Kinetics of the reaction between hydrogen and sulfur under high-temperature Claus furnace conditions," *Industrial & Engineering Chemistry Research*, vol. 29, pp. 2327-2332, 1990.
- [51] L. M. Al-Shamma and S. A. Naman, "Kinetic study for thermal production of hydrogen from H₂S by heterogeneous catalysis of vanadium sulfide in a flow system," *International Journal of Hydrogen Energy*, vol. 14, pp. 173-179, 1989.
- [52] F. Banderhmann and K.-B. Harder, "Production of H₂ via thermal decomposition of H₂S and separation of H₂ and H₂S by pressure swing adsorption," *International Journal of Hydrogen Energy*, vol. 7, pp. 471-475, 1982.
- [53] A. Bishara, O. A. Salman, N. Khraishi and A. Marafi, "Thermochemical decomposition of hydrogen sulfide by solar energy," *International Journal of Hydrogen Energy*, vol. 12, pp. 679-685, 1987.
- [54] B. d. Darwent, R. L. Wadlinger and M. J. Allard, "The photochemical decomposition of hydrogen sulfide. The reactions of hydrogen atoms and HS radicals," *The Journal of Physical Chemistry*, vol. 71, pp. 2346-2347, 1967.
- [55] E. E. Aynsley, T. G. Pearson and P. L. Robinson, "The kinetics of the reaction between hydrogen and sulphur. Part I. Reaction at 265-350 and 290-820 mm," *J. Chem. Soc.*, no. 0, pp. 58-68, 1935.
- [56] M. Randall and F. R. v. Bichowsky, "Equilibrium in the Reaction between Water and Sulfur at High Temperatures. The Dissociation of Hydrogen Sulfide.," *Journal of the American Chemical Society*, vol. 40, pp. 368-375, 1918.
- [57] K. Fukuda, M. Dokiya, T. Kameyama and Y. Kotera, "Catalytic Decomposition of Hydrogen Sulfide," *Industrial & Engineering Chemistry Fundamentals*, vol. 17, pp. 243-248, 1978.
- [58] T. Chivers, J. B. Hyne and C. Lau, "The thermal decomposition of hydrogen sulfide over transition metal sulfides," *International Journal of Hydrogen Energy*, vol. 5, pp. 499-506, 1980.

- [59] H. Tetsuo, S. Ko and Y. Hitoshi, "S₂ Formation during the Pyrolysis of H₂S in Shock Waves," *Bulletin of the Chemical Society of Japan*, vol. 49, pp. 965-968, 1976.
- [60] C. T. Bowman and L. G. Dodge, "Kinetics of the thermal decomposition of hydrogen sulfide behind shock waves," *Symposium (International) on Combustion*, vol. 16, pp. 971-982, 1977.
- [61] D. Woiki and P. Roth, "Kinetics of the High-Temperature H₂S Decomposition," *The Journal of Physical Chemistry*, vol. 98, pp. 12958-12963, 1994.
- [62] H. A. Olschewski, J. Troe and H. G. Wagner, "UV Absorption Study of the Thermal Decomposition Reaction H₂S → H₂ + S(3P)," *The Journal of Physical Chemistry*, vol. 98, pp. 12964-12967, 1994.
- [63] K. Karan, A. K. Mehrotra and L. A. Behie, "On reaction kinetics for the thermal decomposition of hydrogen sulfide," *AIChE Journal*, vol. 45, pp. 383-389, 1999.
- [64] F. Faraji, I. Safarik, O. P. Strausz, E. Yildirim and M. E. Torres, "The direct conversion of hydrogen sulfide to hydrogen and sulfur," *International Journal of Hydrogen Energy*, vol. 23, pp. 451-456, 1998.
- [65] R. B. Slimane, F. S. Lau, M. Khinkis, J. P. Bingue, A. V. Saveliev and L. A. Kennedy, "Conversion of hydrogen sulfide to hydrogen by superadiabatic partial oxidation: thermodynamic consideration," *International Journal of Hydrogen Energy*, vol. 29, pp. 1471-1477, 2004.
- [66] K. Sendt, M. Jazbec and B. S. Haynes, "Chemical kinetic modeling of the H/S system: H₂S thermolysis and H₂ sulfidation," *Proceedings of the Combustion Institute*, vol. 29, pp. 2439-2446, 2002.
- [67] M. Binoist, B. Labégorre, F. Monnet, P. D. Clark, N. I. Dowling, M. Huang, D. Archambault, E. Plasari and P.-M. Marquaire, "Kinetic Study of the Pyrolysis of H₂S," *Industrial & Engineering Chemistry Research*, vol. 42, pp. 3943-3951, 2003.
- [68] R. David and D. Matras, "Règles de construction et extrapolation des réacteurs auto-agités par jets gazeux," *The Canadian Journal of Chemical Engineering*, vol. 53, pp. 297-300, 1975.
- [69] F. Manenti, D. Papasidero and E. Ranzi, "Revised kinetic scheme for thermal furnace of sulfur recovery units," *Chemical Engineering Transactions*, vol. 32, pp. 1285-1290, 2013.
- [70] E. Ranzi, A. Sogaro, P. Gaffuri, G. Pennati and T. Faravelli, "A Wide Range Modeling Study of Methane Oxidation," *Combustion Science and Technology*, vol. 96, pp. 279-325, 1994.
- [71] C. L. Rasmussen, P. Glarborg and P. Marshall, "Mechanisms of radical removal by SO₂," *Proceedings of the Combustion Institute*, vol. 31, pp. 339-347, 2007.

- [72] K. Karan, A. K. Mehrotra and L. A. Behie, "A high-temperature experimental and modeling study of homogeneous gas-phase COS reactions applied to Claus plants," *Chemical Engineering Science*, vol. 54, pp. 2999-3006, 1999.
- [73] T. Y. Cong, A. Raj, J. Chanaphet, S. Mohammed, S. Ibrahim and A. A. Shoaibi, "A detailed reaction mechanism for hydrogen production via hydrogen sulphide (H₂S) thermolysis and oxidation," *International Journal of Hydrogen Energy*, vol. 41, pp. 6662-6675, 2016.
- [74] H. I. Waterman and C. Van Vlodorp, "The preparation of carbon disulphide from methane and hydrogen sulphide," *Journal of the Society of Chemical Industry*, vol. 58, p. 109, 1939.
- [75] E. J. Erekson and F. Q. Miao, "Gasonline from Natural Gas by Sufur Processing," Chicago, 1996.
- [76] C. Huang and A. T-Raissi, "Liquid hydrogen production via hydrogen sulfide methane reformation," *Journal of Power Sources*, vol. 175, pp. 464-472, 2008.
- [77] C. Huang and A. T-Raissi, "Thermodynamic analyses of hydrogen production from sub-quality natural gas: Part I: Pyrolysis and autothermal pyrolysis," *Journal of Power Sources*, vol. 163, pp. 645-652, 2007.
- [78] S. K. Megalofonos and N. G. Papayannakos, "Hydrogen production from natural gas and hydrogen sulphide," *International Journal of Hydrogen Energy*, vol. 16, pp. 319-327, 1991.
- [79] K. Karan and L. A. Behie, "CS₂ Formation in the Claus Reaction Furnace: A Kinetic Study of Methane–Sulfur and Methane–Hydrogen Sulfide Reactions," *Industrial & Engineering Chemistry Research*, vol. 43, pp. 3304-3313, 2004.
- [80] G. P. Towler and S. Lynn, "Development of a zero-emissions sulfur-recovery process. 1. Thermochemistry and reaction kinetics of mixtures of hydrogen sulfide and carbon dioxide at high temperature," *Industrial & Engineering Chemistry Research*, vol. 32, pp. 2800-2811, 1993.
- [81] K. Karan, A. K. Mehrotra and L. A. Behie, "COS-Forming Reaction between CO and Sulfur: A High-Temperature Intrinsic Kinetics Study," *Industrial & Engineering Chemistry Research*, vol. 37, pp. 4609-4616, 1998.
- [82] K. Karan, A. K. Mehrotra and L. A. Behie, "Use of new reaction kinetics for COS formation to achieve reduced sulfur emissions from claus plants," *The Canadian Journal of Chemical Engineering*, vol. 77, pp. 392-398, 1999.
- [83] N. AuYeung and A. F. T. Yokochi, "Steam reformation of hydrogen sulfide," *International Journal of Hydrogen Energy*, vol. 38, pp. 6304-6313, 2013.
- [84] P. Sadooghi and R. Rauch, "Experimental and modeling study of hydrogen production from catalytic steam reforming of methane mixture with hydrogen sulfide," *International Journal of Hydrogen Energy*, vol. 40, pp. 10418-10426, 2015.
- [85] M. Dokiya, K. Fukuda, H. Yokokawa and T. Kameyama, "The Study of Thermochemical Hydrogen Preparation. VI. A Hydrogen-Evolving Step

- through the H₂S-CO Cycle," *Bulletin of the Chemical Society of Japan*, vol. 51, no. 1, pp. 150-153, 1978.
- [86] M. Sugioka and K. Aomura, "A possible mechanism for catalytic decomposition of hydrogen sulfide over molybdenum disulfide," *International Journal of Hydrogen Energy*, vol. 9, pp. 891-894, 1984.
 - [87] T. Kameyama, M. Dokiya, M. Fujishige, H. Yokokawa and K. Fukuda, "Production of hydrogen from hydrogen sulfide by means of selective diffusion membranes," *International Journal of Hydrogen Energy*, vol. 8, pp. 5-13, 1983.
 - [88] D. J. Edlund and W. A. Pledger, "Catalytic platinum-based membrane reactor for removal of H₂S from natural gas streams," *Journal of Membrane Science*, vol. 94, pp. 111-119, 1994.
 - [89] D. Edlund, D. Friesen, B. Johnson and W. Pledger, "Hydrogen-permeable metal membranes for high-temperature gas separations," *Gas Separation & Purification*, vol. 8, pp. 131-136, 1994.
 - [90] D. J. Edlund and W. A. Pledger, "Thermolysis of hydrogen sulfide in a metal-membrane reactor," *Journal of Membrane Science*, vol. 77, pp. 255-264, 1993.
 - [91] T. Nishizawa, H. Tanaka and K. Hirota, "Decomposition of hydrogen sulfide and enrichment of the hydrogen produced by the use of thermal diffusion columns," 1979.
 - [92] H. Selim, A. K. Gupta and A. A. Shoaibi, "Effect of CO₂ and N₂ concentration in acid gas stream on H₂S combustion," *Applied Energy*, vol. 98, pp. 53-58, 2012.
 - [93] H. Selim, A. A. Shoaibi and A. K. Gupta, "Effect of H₂S in methane/air flames on sulfur chemistry and products speciation," *Applied Energy*, vol. 88, pp. 2593-2600, 2011.
 - [94] H. Selim, S. Ibrahim, A. A. Shoaibi and A. K. Gupta, "Effect of oxygen enrichment on acid gas combustion in hydrogen/air flames under claus conditions," *Applied Energy*, vol. 109, pp. 119-124, 2013.
 - [95] H. Selim, A. A. Shoaibi and A. K. Gupta, "Fate of sulfur with H₂S injection in methane/air flames," *Applied Energy*, vol. 92, pp. 57-64, 2012.
 - [96] S. Ibrahim, A. A. Shoaibi and A. K. Gupta, "Effect of benzene on product evolution in a H₂S/O₂ flame under Claus condition," *Applied Energy*, vol. 145, pp. 21-26, 2015.
 - [97] S. Ibrahim, A. A. Shoaibi and A. K. Gupta, "Xylene addition effects to H₂S combustion under Claus condition," *Fuel*, vol. 150, pp. 1-7, 2015.
 - [98] S. Ibrahim, A. A. Shoaibi and A. K. Gupta, "Role of toluene in hydrogen sulfide combustion under Claus condition," *Applied Energy*, vol. 112, pp. 60-66, 2013.
 - [99] S. Ibrahim, A. A. Shoaibi and A. K. Gupta, "Role of toluene to acid gas (H₂S and CO₂) combustion in H₂/O₂-N₂ flame under Claus condition," *Applied Energy*, vol. 149, pp. 62-68, 2015.

- [100] M. Yumura and E. Furimsky, "Hydrogen sulphide adsorption and decomposition in the presence of manganese nodules," *Applied Catalysis*, vol. 16, pp. 157-167, 1985.
- [101] O. A. Salman, A. Bishara and A. Marafi, "An alternative to the claus process for treating hydrogen sulfide," *Energy*, vol. 12, pp. 1227-1232, 1987.
- [102] T. Chivers and C. Lau, "The thermal decomposition of hydrogen sulfide over alkali metal sulfides and polysulfides," *International Journal of Hydrogen Energy*, vol. 10, pp. 21-25, 1985.
- [103] H. Kiuchi, K. Funaki and T. Tanaka, "Thermochemical decomposition of hydrogen sulfide with nickel sulfide," *Metallurgical Transactions B*, vol. 14, pp. 347-352, 1983.
- [104] L. M. Al-Shamma and S. A. Naman, "The production and separation of hydrogen and sulfur from thermal decomposition of hydrogen sulfide over vanadium oxide/sulfide catalysts," *International Journal of Hydrogen Energy*, vol. 15, pp. 1-5, 1990.
- [105] T. V. Reshetenko, S. R. Khairulin, Z. R. Ismagilov and V. V. Kuznetsov, "Study of the reaction of high-temperature H₂S decomposition on metal oxides (γ -Al₂O₃, α -Fe₂O₃, V₂O₅)," *International Journal of Hydrogen Energy*, vol. 27, pp. 387-394, 2002.
- [106] W. M. Kays, M. E. Crawford and B. Weigand, *Convective Heat and Mass Transfer*, New York: McGraw-Hill, 2005.
- [107] "Chemical Equilibrium with Application," Nasa - Glenn Research Center, [Online]. Available: <https://www.grc.nasa.gov/WWW/CEAWeb/>.
- [108] V. P. Nguyen, V. Burklé-Vitzthum, P. M. Marquaire and R. Michels, "Pyrolysis mechanism of the n-octane/H₂S mixture at 70 MPa and 603–623 K," *Journal of Analytical and Applied Pyrolysis*, vol. 113, pp. 46-56, 2015.
- [109] I. A. Gargurevich, "Hydrogen Sulfide Combustion: Relevant Issues under Claus Furnace Conditions," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 7706-7729, 2005.
- [110] V. Palma, V. Vaiano, D. Barba, M. Colozzi, E. Palo, L. Barbato and S. Cortese, "H₂ production by thermal decomposition of H₂S in the presence of oxygen," *International Journal of Hydrogen Energy*, vol. 40, pp. 106-113, 2015.
- [111] V. Poloczek and H. Hermsmeyer, "Modern gas turbines with high fuel flexibility," *POWER-GEN Asia, Kuala Lumpur, Malaysia*, 2008.
- [112] H. S. F. Chin, K. Karan, A. K. Mehrotra and L. A. Behie, "The fate of methane in a claus plant reaction furnace," *The Canadian Journal of Chemical Engineering*, vol. 79, pp. 482-490, 2001.
- [113] D. L. Baulch, C. J. Cobos, R. A. Cox, P. Frank, G. Hayman, T. Just, J. A. Kerr, T. Murrells, M. J. Pilling, J. Troe, R. W. Walker and J. Warnatz, "Evaluated Kinetic Data for Combustion Modeling. Supplement I," *Journal of Physical and Chemical Reference Data*, vol. 23, pp. 847-848, 1994.

- [114] V. Y. Basevich, V. I. Vendeneev and V. S. Arutyunov, "Modeling of laminar hydrogen sulfide and carbon disulfide flames," *Chem. Phys. Repts*, vol. 13, 1995.
- [115] Reaction Design, *ANSYS CHEMKIN 17.0(15151)*, San Diego, 2016.
- [116] C. Huang and A. T-Raissi, "Thermodynamic analyses of hydrogen production from sub-quality natural gas: Part II: Steam reforming and autothermal steam reforming," *Journal of Power Sources* , vol. 163, pp. 637-644, 2007.

LIST OF PUBLICATIONS

JOURNAL PAPERS

[1] El-Melih, A. M., Ibrahim, S., Al Shoaibi, A., and Gupta, A. K., “Experimental Examination of Syngas Recovery from Acid Gases”, *Applied Energy*, 164 (2016), pp. 64 - 68.

[2] El-Melih, A. M., Al Shoaibi, A., and Gupta, A. K., “Hydrogen Sulfide Reformation in the Presence of Methane,” *Applied Energy*, 178 (2016), pp. 609 - 615.

[3] El-Melih, A. M., Al Shoaibi, A., and Gupta, A. K., “Production of Hydrogen Sulfide in Presence of Methane,” *International Journal of Hydrogen Energy*, 42, (2017), pp. 4764 - 4773.

[4] El-Melih, A. M., Al Shoaibi, A., and Gupta, A. K., “Reformation of Hydrogen Sulfide to Hydrogen in the Presence of Xylene,” *Applied Energy*, 203, (2017), pp. 403 - 411.

CONFERENCE PAPERS

[1] Commenges. J., El-Melih, A. M., and Gupta, A. K., “Simulation and Validation of Hydrogen Sulfide Production from Hydrogen Sulfide Pyrolysis,” *Proceedings of the ASME 2016 Power & Energy Conference, PowerEnergy 2016-59036*, June 26 – 30, 2016, Charlotte, North Carolina.

[2] El-Melih, A. M., Ibrahim, S., Al Shoaibi, A., and Gupta, A. K., “Reactor Parameters Effects on Hydrogen Production from Hydrogen Sulfide,” *14th AIAA International Energy Conversion Engineering Conference (IECEC)*, Salt Lake City, UT, July 25-27, 2016, AIAA 2016-4952.

- [3] El-Melih, A. M., Al Shoaibi, A., and Gupta, A. K., “Effect of Oxygen Injection on Hydrogen Sulfide Pyrolysis,” Proceedings of the ASME 2017 Power & Energy Conference, PowerEnergy 2017-3791, June 26 – 30 , 2017, Charlotte, North Carolina.
- [4] El-Melih, Al Shoaibi, A., and Gupta, A. K., “Production of Hydrogen from Hydrogen Sulfide Reformation in the Presence of Benzene,” 15th AIAA International Energy Conversion Engineering Conference (IECEC), Atlanta, GA, July 10-12, 2017, AIAA 2016-2709193.